TEXTILE RESEARCH JOURNAL

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MARCH 1961

One of a series

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IN THIS ISSUE

Cotton Quality Study VI. Wrinkle Resistance and Recovery from Deformation. *Henry Tovey* 185

Response of Cottons to Chemical Treatments. Part II: Yarn Mercerization. *L. Rebenfeld* 253

The Reactivity of Some Epoxides toward Cellulose. *Richard Steele* 257

Fluorescent Brightening Agents: Their Photodecomposition in Aqueous Solution and on Substrate and Phototendering Activity for Cellulose. *E. H. Daruwalla and C. I. Peter* 263

The Improvement of the Wrinkle Recovery of Cotton by Reaction with Formaldehyde. *S. J. O'Brien and W. J. van Loo, Jr.* 276

REPRINT REQUESTS SHOULD BE DIRECTED TO THE AUTHORS
SEE ARTICLES FOR ADDRESSES

Cotton Quality Study VI: Wrinkle Resistance and Recovery from Deformation, by Henry Tovey

Table of Contents

Introduction 185

The Cotton Fiber 186

The Cellulose Chain and Intermolecular Forces . 186
Crystallinity and Lateral Order 186
Fiber Structure 187

Deformation and Recovery in Cotton 189

Direction of Stress 190
Magnitude of Stress 190
Duration of Stress 191
Environmental Factors 191
Mechanisms of Cotton's Deformation and Recovery 192

Improvement of Cotton's Wrinkle and Deformation Recovery: Mechanisms 192

Mode of Action of Treating Agents 192
Level of Deformation Recovery 194
Structure and Size of Cross-Linkages 196
Distribution of Cross-Linkages 197
Dry and Wet Wrinkle Resistance 198
Finish Durability 199
Strength Losses 201
Action of External Agents 202

Improvement in Cotton's Wrinkle and Deformation Recovery: Materials 202

Materials (Formaldehyde and other aldehydes, Acetals, Methylol urea compounds, Cyclic methylol urea compounds, Triazones, Methylol melamine compounds and triazines, Epoxides and related compounds, Multipurpose finishes, Other creaseproofing agents) 202
Catalysts 206
Side Effects (Chlorine damage, Odor formation, Lightfastness of dyes) 206

Improvement in Cotton's Wrinkle and Deformation Recovery: Processes 208

Conventional Method 209
The Wet-Cure Process 210
Processing of Knit Goods 210
Pleating 210
Surface Effects 211

Yarn and Fabric Construction 211

Fiber Properties 211
Yarn Construction 212
Fabric Construction 212

Testing Methods and Equipment 213

Mechanical Properties 213
Wrinkle Recovery 214
Appearance Tests 216
Crease Retention 220

Research Opportunities 220

The Cotton Fiber 221
Deformation and Recovery in Cotton 221
Improvement in Cotton's Deformation and Recovery: Mechanisms 221
Materials 223
Processing 224
Yarn and Fabric Construction 224
Testing 224
Durable Creases 225
New Products 226

Literature Cited 227

MARCH 1961
VOL. 31 NO. 3

TEXTILE RESEARCH JOURNAL

Cotton Quality Study VI

Wrinkle Resistance and Recovery from Deformation

Henry Tovey

National Cotton Council of America, Utilization Research Division, Washington, D. C.

Introduction

Wrinkle resistance has been defined as that property of a fabric which causes it to recover from folding deformations. In cotton, improvements in this property are obtained by chemical finishes which improve the ability of fibers to maintain configurations in which they are treated. The fabrics are finished in the piece, when they are flat and smooth. The high degree of recovery from deformation imparted to fibers allows fabrics to recover from wrinkling and maintain smooth appearance.

The first attempts to improve cotton fabric recovery from wrinkling by chemical finishing date back to the 1920's [229, 230, 231, 232]. However, undesirable side effects of the treatment prevented its commercial utilization at that time. Further work on the process succeeded in improving the products, but progress was slow. Considerably less than 1% of cotton fabric production was finished for wrinkle resistance in 1948 [110]. The great acceleration in the pace of research and development came in the early years of the past decade. It became apparent at that time that the increased deformation recovery of creaseproofed fabrics also helps them to dry to a smooth state after laundering—that the treatment imparts not only the ability to recover from wrinkles imposed by wear but also from wrinkles imposed in laundering. Spurred by claims made for synthetic fiber fabrics, research aimed at the development of wash-and-wear cottons was intensified. By 1955 they appeared on the market in volume.

Wrinkle-resistant wash-wear cottons combine the traditional comfort, washability, and economy of the native fiber with easy-care properties desired in many textiles today. As a result, they enjoy excellent consumer acceptance. In 1955, the first year in which production reached a significant volume, 600 million linear yards of cotton fabrics were treated for wrinkle resistance. Three years later, in 1958, production reached 1.5 billion linear yards, and 1.9 billion yards of wash-wear cottons were produced in 1959 [459, 784].

The importance of the wash-wear market to the cotton industry, textile finishers, and chemical suppliers is apparent from the production figures. The cost of finishing for easy-care adds 3–4¢/yd. to the usual finishing costs. A significant portion of this increase goes to pay the bill for chemicals required for the treatment. These materials constitute about 4–5% of finished fabric weight. On the basis of the 1.9 billion yards figure, and assuming an average finished fabric weight of 5 oz./yd., the cotton finishing industry used in 1959 about 30 million pounds

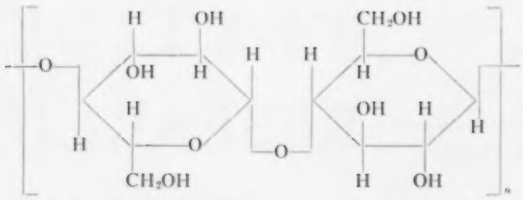

Fig. 1. The repeating unit of cellulose is the cellobiose group, made up of two anhydroglucose rings linked through an oxygen bridge.

of creaseproofing compounds (on 100% solids basis) plus catalysts and auxiliary chemicals such as softeners. Actually, because of losses in chemicals during the treatment, purchases were considerably higher.

The continued success enjoyed by wrinkle-resistant cottons augurs well for the future. The figure of 1.9 billion yards for 1959 represents 63% of total production of easy-care fabrics, including synthetics and blends. This is only 26% of the total textile market in which wrinkle resistance and easy-care properties are important. The other 74% represents a potential market of over 5 billion yards of fabric and considerably more than 100 million pounds of chemicals.

In addition, more extensive utilization of improvements in cotton's deformation recovery can open new markets for cotton and for the chemicals needed for the treatments. Retention of smooth appearance is the only property of interest to consumers produced by such treatments which has been exploited extensively to date. Improvements in cotton's recovery from deformation, however, can also lead to products with other desirable end-use qualities. For example, it should be possible to produce lofty cotton fabrics which are warm and yet not heavy, and which maintain their loftiness through many wash-and-use cycles. Since cotton holds a substantial price advantage over competing materials in end uses in which warmth is important, improvements in this property would permit it to capture a larger share of this 1,383 million pounds a year market than its present 40% [458].

Continued increase in sales of wrinkle-resistant cottons depends largely on continued improvement in the quality of the goods. This, in turn, depends on more complete understanding of the chemical and physical processes involved and on development of improved finishing methods and materials. Much new information on this subject has been obtained since 1949, when the Council's first study on crease resistance was published [110]. The present study reviews this information and proposes topics for needed research.

The Cotton Fiber

A fiber's recovery from deformation is a function of its composition and structure. Cotton is composed mainly of cellulose, and in many ways it resembles other cellulosic fibers, such as ramie, linen, and rayon. However, cotton's response to stress is unlike that of other cellulosic fibers because of the unique spatial arrangement of its molecules.

The Cellulose Chain and Intermolecular Forces

Chemically, the mature cotton fiber is almost pure cellulose, with pectin, waxes, proteins, sugar, ash, and organic acids comprising less than 5% of its weight. These compounds are largely removed by initial finishing processes and have little effect on the mechanical properties of finished cotton products.

The building blocks of cellulose molecules are anhydroglucose rings, which are connected to each other by glycosidic linkages (Figure 1). The number of anhydroglucose rings in a cotton cellulose molecule has been estimated to average about 5000 [491, 723].

Although cellulose chains may be linked to each other to some extent by primary valence bonds [529, 530, 625], it is generally believed that the molecules are held together mainly by secondary forces. The symmetry and regularity of cellulose molecules permit adjacent chains to pack closely, and the lack of bulky substituents on chains favors development of intermolecular forces which would be ineffective at larger distances. Van der Waals' forces augment cohesion resulting from hydrogen bonds formed between the many hydroxyl groups on the molecules.

Crystallinity and Lateral Order

Some regions of the fiber are capable of diffracting X-rays in the same manner as three-dimensional crystal lattices, and these regions are often called crystalline. The extent of crystallinity in cotton, as determined by X-ray methods, is about 70–80% [640, 744]. This figure may be too low, since much more X-ray scattering previously attributed to disordered matter may be attributable to crystal reflections [268].

Attempts to determine crystallinity by chemical methods were based on the assumption that hydroxyl groups in crystalline regions are not available for chemical reactions. The hydroxyls found reactive were apportioned between amorphous cellulose and surfaces of crystallites [338].

Characterization of cellulose as either crystalline or amorphous is an oversimplification. In some fiber regions the molecular arrangement is neither completely random nor perfectly regular. Hydroxyl groups in these regions are available to some reagents and not to others, and the same regions behave as if they were amorphous in one experiment and as if they were crystalline in another. The number of hydroxyls found available varies with reaction conditions, reagents used, and the history of the fiber [402, 643, 726]. The various methods give different results because for each there is a different degree of order which constitutes the dividing line between the crystalline and the amorphous. Accordingly, it has been proposed that cellulose be characterized by the perfection of lateral order of the chain molecules. However, cotton, unlike regenerated cellulosic fibers, shows the presence of little matter of intermediate degree of order. The bulk of cotton cellulose appears to be of high order and much of the rest of low order (Figure 2) [425].

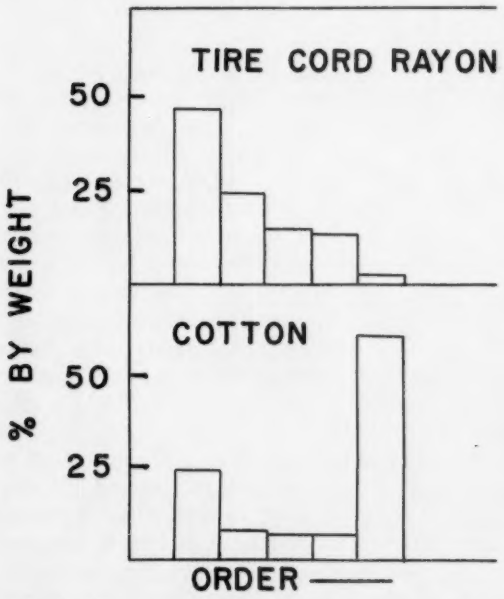

Fig. 2. Histogram plot of mass-order distribution from NO_2 oxidation. The bulk of cotton cellulose appears to be of high, and much of the rest of low order.

Fiber Structure

Gross structure. On examination with the optical microscope, the mature cotton fiber resembles a collapsed, twisted tube with comparatively thick walls (Figure 3) [601]. Length, thickness, and extent of twist differ widely for different varieties of cotton, for cotton grown under different conditions, and even for fibers from the same boll. The staple length of cotton in commerce varies from ¾ to 1¾ in., and the fiber is approximately 3000 times as long as it is wide. The absolute twist is nearly zero, because the number of Z-turns about equals the number of S-turns [134].

On the outside of the fiber there is a thin, skinlike sheath of cellulose strands impregnated with waxes, pectins, and nitrogenous materials (Figure 4); it is called the primary wall. Underneath is the secondary wall, which constitutes the main body of the fiber. It is composed of 25–40 concentric layers of threadlike fibrils arranged spirally about the long axis of the fiber. The X-ray angle, a measure of the angle the spirals make with the axis, varies for different cottons, averaging about 30° [723]. The direction of the spirals reverses 25–50 times per inch. The reversals seem to occur at approximately the

Fig. 3. On examination with the optical microscope, mature cotton fibers resemble collapsed, twisted tubes with comparatively thick walls.

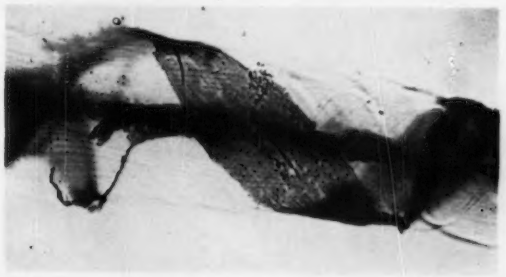

Fig. 4. Primary wall, winding layer, secondary wall, and lumen are discernible on fibers swollen with cuprammonium hydroxide.

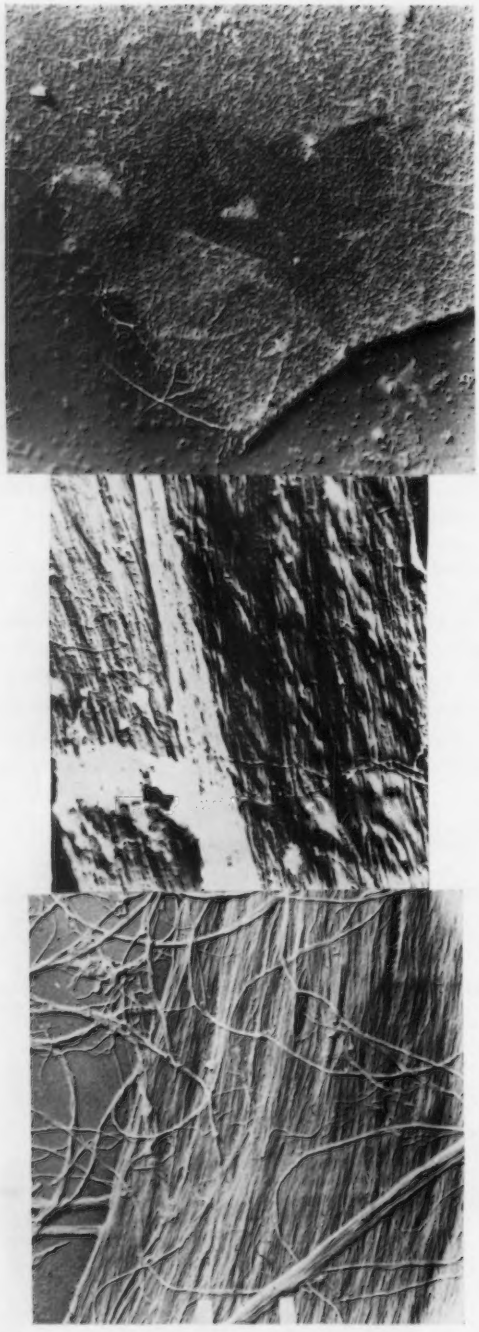

Fig. 5. Electron microscopy provides much detail about the fine structure of cotton. Top to bottom: Purified primary wall, winding layer, sheet of secondary wall.

same points along the length of the fiber in all layers, i.e., are more or less continuous along the plane of a cross section [525]. In the center of the fiber the lumen holds the dried-up remains of the protoplasm of the living cotton cell [121]. In mature cotton the lumen is collapsed and almost invisible.

Measurements of the density of cotton, and other experimental evidence, testify to the existence of a system of empty spaces throughout the fiber [642, 741].

Fine structure. Electron microscopy provides much more detail about the fine structure of cotton (Figure 5) [376, 600, 601, 719, 720]. The cellulosic component of the primary wall consists of a network of interweaving fibril strands, 100–400 Å in diameter, running parallel to the fiber axis on the outside and transverse on the inside. The outermost layer of the secondary wall, called the winding layer, is a continuous sheet made up of alternating narrow and wide bands of fibril bundles about 1000 Å thick, spiralling about the fiber axis. The other layers of the secondary wall are composed of highly packed spirals of microfibrils. The individual layers are about 1000 Å, or 5 microfibrils thick.

The microfibrils are believed to consist of bundles of cellulose molecules. The smallest microfibrils observed are a few hundred angstroms in diameter. But even the electron microscope does not show exactly how the molecules are arranged within the fibrils. It is not known whether the microfibrils are predominantly crystalline or contain appreciable amounts of disordered matter. It is not known whether there is cellulosic matter between the fibrils at all, and, if there is, whether it consists of molecules which stray from one microfibril and join another or of cellulose molecules which never become a part of a fibril. Several structures have been proposed (Figure 6), and while none is fully consistent with all experimental evidence, the concept of a highly crystalline core surrounded by a paracrystalline mantle has been found useful [134, 234, 311, 321, 330, 643, 719, 721].

Formation of the cotton fiber. The fiber starts to grow from an epidermal cell on the seed. It continues to grow for about 18 days, when it reaches nearly its eventual length. Cellulose is deposited on the inside walls of the cell, forming concentric layers which are easily discernible on photographs of cross sections of swollen fibers (Figure 7) [63]. This "growth ring" structure is absent in fibers

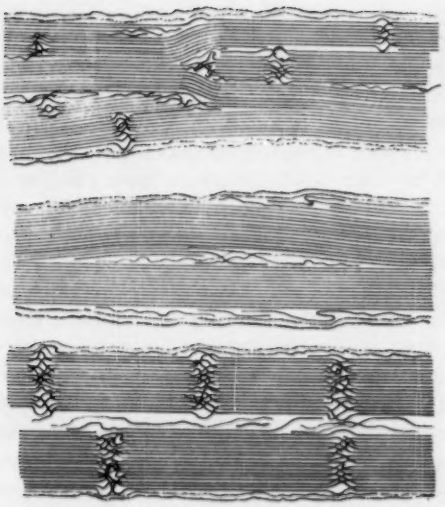

Fig. 6. Schematic diagram of three suggested arrangements of cellulose chains in microfibrils.

grown under continuous light and even temperatures, and has been ascribed to differences in the density of day-deposited and night-deposited layers [20, 375]. Exactly how cellulose is formed and deposited on the cell wall is not known.

While the cellulose molecule could be thought of as a condensation polymer, formed by addition of glucose on both ends of the growing chain, there is some evidence that it grows at one end only, from the root up, with the growing end imbedded in the protoplasm of the cell as a hair root in skin [551]. Enzymes in the cell may have the power of adding monomeric molecules to the chains in a particular order, generating the regular chain molecules of cellulose.

The picture of a cellulose molecule growing out of the protoplasm of the cell has much to offer in explaining the very highly ordered fibrillar structure of the cotton fiber. The molecules, growing side by side, could come very close to each other before they would develop the kinks and loops normally present in free long molecules. They could thus be contiguous along large portions of their entire length, and hydrogen bonds could form between them. Since there are no bulky substituents on the chains, packing would not be hindered sterically. The regular syndiotactic structure of the molecules would favor the formation of highly crystalline microfibrils. However, why the microfibrils spiral about the fiber

Fig. 7. Cellulose is deposited on the inside walls of the cell, forming concentric layers which are easily discernible on photographs of cross sections of swollen fibers.

axis, and why in cotton—and in cotton alone of all the cellulosic fibers—the spirals reverse their direction is as much a mystery today as it was when first observed.

Deformation and Recovery in Cotton

When a stress is applied to a textile product, as in wrinkling, it is transferred to the component fibers. The degree of stress transfer is a function of the geometry of the system, but the response of the textile to the stress, in the final analysis, depends on the response of the individual fibers [166, 467, 700].

Each structural element of the cotton fiber—a molecule, a crystallite, a microfibril—is subject to many forces differing in strength and in direction: Van der Waals' forces, hydrogen bonds, and primary valence bonds. The configuration of these elements, hence the form of the fiber, is that in which the various forces balance each other. When an external stress is applied to the system it disturbs the equilibrium. The bonds take up the stress and strain, and some bonds break. The elements align themselves in the direction of the stress. If they come into the proximity of other elements, they may form new bonds with their new neighbors. Under continuing stress, these processes continue until the fiber fails or a new equilibrium configuration, in which the various forces again balance each other, is achieved. The external load is a part of the new equilibrium, since the fiber deforms until the load is balanced by the strain on bonds between its elements.

Upon removal of the external load, the equilibrium will once more be disturbed. The strains on bonds will no longer be balanced, and processes aimed at restoring an equilibrium will therefore be immediately activated. These processes will continue until the elements again acquire a configuration in which the various forces balance each other. Just how nearly this eventual configuration will resemble the original one—how complete will be the recovery—depends on the direction, magnitude, and duration of the stress to which the fiber was subjected, and on environmental factors.

Direction of Stress

The determination of effects of a stress applied to a fiber in directions other than its length is difficult. Therefore, most available data come from experiments in which the fiber is elongated under tension and then permitted to recover. The information obtained from these experiments seems to apply to the creasing behavior of a fabric. In a sharply folded fabric the fibers within the fold are bent. Each bent fiber is subjected to tensile stress, which acts on the section of the fiber on the outside of the bend and forces it to elongate, and to compressive stress, which acts on the region inside the bend and forces it to contract. While the direction of the compressive force is opposite to that of tension, the structural elements of the fiber are believed to deform by similar mechanisms.

The equivalence of the tensile and compressive forces holds strictly true for systems in which stress gives rise to viscoelastic processes alone. This is not precisely the case in cotton fibers, whose component fibrils appear to buckle under compression [722], much as individual fibers in loosely twisted yarns do when the yarns are bent. This phenomenon does not have a counterpart in the region of tensile stress. It is likely that stresses applied in a direction other than the long axis of the fiber, as for example in torsion, may have still different effects. However, little work has been done on these problems [56, 472].

Magnitude of Stress

The importance of the magnitude of stress is apparent. The higher the stress on bonds, the more they will stretch and break, and the greater will be slippage between structural elements of the fiber and deformation.

The deformation of a cotton fiber under stress takes place by stretching of bonds and slippage between its structural elements. The extension due to bond stretching is recoverable. However, a part of the stress energy is lost in the process, and the recovery force of the strained bonds may be counteracted by other bonds formed between the straightened and aligned structural elements of the fiber. The extension due to slippage of fiber elements past each other is largely not recoverable.

When a cotton fiber is stretched, the angle that fibrils make with the fiber axis decreases [156, 646]. The fiber appears to elongate by extension of the spiral structure of the fibrils. In fact, the extensibility of the fiber depends on the angle the fibrils make with the fiber axis; fibers in which the angle is high are capable of larger extension than those in which the angle is low to start with. However, permanent set is also a function of the spiral angle. Cottons with high angles are more extensible but exhibit less elastic recovery [320, 468, 563, 565]. Apparently, once slippage at fibril interfaces takes place and the fibrils become well aligned and contiguous, they can no longer return to their original configuration.

When a cotton fiber is stretched once and permitted to recover freely, it is harder to stretch the second time, its extensibility is decreased, and its elastic recovery is improved [102]. The changed properties of a mechanically conditioned fiber can be ascribed to decreased contribution of slippage to the fiber's response to stress. Extension of mechanically conditioned fibers is afforded primarily by bond stretching, which is recoverable. It appears, therefore, that improved deformation recovery can be obtained by reducing interfibrillar and intermolecular slippage in fibers' response to stress.

The stress magnitude also determines through which structural elements the fiber responds to stress, because bonds of different strengths respond differently to a stress of a given magnitude. Thus a group of cellulose chains can respond to stress as a unit if the molecules within it are bound to each other by very strong forces, and if the group as a whole is connected to other elements of the fiber by weaker bonds. At the same time, there may be changes in the shape of the group-unit. At a given stress, bonds within it may be affected less than those connecting it to other elements, but they will be affected to some extent. A fibril under stress

may bend as a unit, but the bonds between and within the molecules comprising it will also strain.

Effect of lateral order. Cellulose molecules in a crystallite are both parallel and close to each other, and the bonds which connect them are numerous. If stress is applied, all the bonds will share it, and those within a class, as for example all the hydrogen bonds of equal lengths, will share the load equally. Any given magnitude of stress will give rise to a certain corresponding strain on each bond, and each bond will be stretched to the same extent. To separate the molecules, therefore, the stress must be high enough to overcome the strength of all the bonds acting in concert—it must be higher than the sum of their strengths.

In the less ordered regions the molecules are neither so close to each other nor parallel. Because intermolecular forces can develop only if distances between molecules are small enough, and because strength of intermolecular forces varies with distance, bonds between molecules in disordered regions are neither numerous nor uniform in strength. Stress applied to such a system cannot be shared by all bonds equally. The bonds along which the lines of force form will bear the brunt of the load. Molecules in disordered regions can be pulled apart at lower stress than those in the crystalline regions, and the change in the configuration of disordered structures at any given stress is much larger than in ordered regions.

It has been suggested that in cotton fibers extension is accompanied by untwisting of the fibrillar spirals, the S-twisted spiral sections rotating in one direction and the Z-twisted spiral sections turning in the opposite direction [189, 523, 525]. The points of spiral reversals, which seem more nearly crystalline than all other areas in the fiber [742, 743], serve as anchor points about which the rotation occurs. Cotton is the only fiber in which the direction of microfibrillar spirals reverses, and this mechanism may be responsible for its comparatively high extensibility, which is about twice that exhibited by such other highly crystalline natural cellulosic fibers as flax.

The deformation of microfibrils required for their extension and rotation may be afforded by bond stretching, possibly aided by molecular slippage within the fibrils. However, this would require a much more extensive disruption of the structure between fibrils in the fiber regions in which there exists the greatest molecular disorder. It is likely that it is in these regions, on and in between the surfaces of fibrils, that much of the bond breaking, slippage and flow of chains, and new bond formation takes place [679].

Duration of Stress

While at a given stress level the change in the disordered structure is larger than that in ordered regions, it is much more time dependent [469, 660]. Where the bonds share the load equally, once the load is high enough they all break at once. This is a "go–no go" situation, and whether the molecules are pulled apart or not depends only on the magnitude of the stress. Where load-sharing is limited, however, the bonds fail one by one. Here the deformation depends not only on magnitude of stress but also on its duration. The breaking of a bond takes time—a very short time, to be sure, but it does not happen instantaneously. For each individual bond the stressing process consists of a gradual build-up of strain, sometimes culminating in failure, sometimes not, depending on the strength of the bond and the magnitude of stress. For the fiber, however, only the sum of all these processes is apparent, and it appears as continuing deformation or *creep*. The deformation is decelerating continuously, because as time passes a larger proportion of the stress is taken up by bonds which can support the strain without breaking, and there is consequently less and less bond breakage, slippage, and flow.

Delayed recovery is another manifestation of the same time-dependent process. When an applied stress is removed, a part of the deformation is recovered immediately, but the recovery continues for a long time thereafter. The energy stored in bonds strained originally by the stress keeps the fiber elements moving.

Environmental Factors

Humidity. Of environmental factors influencing deformation and recovery of cotton, the most important is humidity [312, 314]. The fiber is easily penetrated by moisture, and its moisture content, often expressed as *regain* or percent of the bone-dry weight, varies with humidity. Water is adsorbed readily on hydroxyl groups and, since it can break hydrogen bonds between them, the degree of freedom and the mobility of fiber structural elements

increase with humidity. Consequently, the dry, strongly hydrogen-bonded fiber has a higher initial modulus, lower extensibility, and higher deformation recovery than the water-lubricated, more flexible, wet fiber [264, 470]. Stress relaxation is also more rapid at higher moisture regain, again presumably because of this internal lubricating effect [19].

Temperature. Temperature seems to have little effect on cotton's deformation and recovery. Stress relaxation has been found to be more rapid at higher temperatures, but the change is small [114]. The forces between cellulose molecules in dry cotton are so strong that the fiber exhibits neither thermoplasticity nor second-order transition temperature [103]. The amount of energy required to break the intermolecular bonds is apparently so high that the molecules decompose before second-order transition is reached.

Mechanisms of Cotton's Deformation and Recovery

On the basis of the foregoing considerations, the deformation by which a native cotton fiber responds to stress can be attributed to extension of its fibril structure, made possible by changes in valence bond angles and bond stretching within fibrils, and by slippage at fibril interfaces and within fibrils if they are not fully crystalline. The slippage is associated with bond breaking and molecular flow, and is accompanied by formation of new bonds between fibrils and between molecules in the stressed configuration. Recovery is due primarily to the energy stored in the strained bonds; it is aided by thermal motion of the molecules. Return to the prestressed configuration is incomplete because it is opposed by the new bonds and because a part of the stressing force is dissipated as the molecules slip past each other.

Improvement of Cotton's Wrinkle and Deformation Recovery: Mechanisms

In the first chemical creaseproofing process, fabrics were impregnated with resin precondensates, dried, and finally cured at elevated temperatures [230, 231, 232]. The mechanisms through which improvement in deformation recovery was obtained were not well understood at the time, and in spite of considerable effort are not fully understood even today [12, 85, 91, 92, 142, 173, 197, 223, 256, 258, 259, 287, 296, 398, 399, 428, 431, 432, 440, 441, 442, 499, 509, 512, 515, 532, 676, 766].

Mode of Action of Treating Agents

The earliest explanation offered for the achievement of wrinkle resistance by treatment with resin precondensates was the formation of a resilient coating around fibers. However, while some evidence supporting this view has been published [370], it has been shown that under the conditions used in conventional creaseproofing the precondensates do not coat fibers but penetrate them more or less uniformly [141, 748]. It has also been shown that treatments with polymerized compounds, which cannot penetrate the fibers but form resin deposits on fiber surfaces, confer no wrinkle recovery on the fabrics; on the contrary, they make fabrics stiff and more easily wrinkled [258, 512, 519].

Two major theories have been advanced to explain the improved wrinkle recovery of cottons treated with resin precondensates. According to the "deposition" theory, the precondensate forms small resin particles, dispersed in the accessible regions of the fiber. According to the "cross-link" theory, molecules of the creaseproofing agent, which must be at least difunctional, react with hydroxyl groups on cellulose chains and form bridges between them. These bridges, or cross-linkages, are bound to cellulose by true chemical covalent bonds. Many workers believe that both mechanisms may operate simultaneously, with one type of reaction prevailing over the other, depending on the properties of the reagents, type of catalyst, conditions of cure, etc. [119, 255, 399, 463, 464, 499, 512, 515, 605, 748].

The difficulties involved in settling this controversy can be appreciated if it is considered that many different reactions can take place when a treating agent is applied to cotton. A molecule of dimethylol urea, for example, can react in nine different ways [515]. Which, if any, of these nine possible reactions predominates has not been determined with certainty.

The resin deposition theory. The resin deposition theory was suggested by the fact that the early treating agents were resin precondensates which can form three-dimensional polymers under conditions used in treating cotton. However, it was found that many resin formers which are not capable of reaction with cellulose do not improve wrinkle recovery when introduced inside fibers and caused to polymerize [308, 506, 515]. Moreover, acetylated cotton, which cannot be cross-linked because the hydroxyl groups are blocked, shows no improvement in wrinkle resist-

ance on treatment with either resin precondensates or non-resin-forming agents [332].

Another argument advanced in support of the resin-deposition theory is based on the comparative ease with which some precondensates can be stripped from treated fabrics [198]. Formaldehyde, acknowledged to cross-link cellulose, cannot be hydrolyzed as easily. However, susceptibility to hydrolysis depends on the chemical nature of the bond; the bonds formed between N-methylol precondensates and cellulose are easier to hydrolyze than those formed by formaldehyde.

Still, the resin deposition theory has the support of some experimental evidence [3, 118, 207, 257, 324, 463, 515]. Certain precondensates, believed to be incapable of cross-linking cellulose when applied with alkaline catalysts, have been found to improve wrinkle recovery. However, the improvement obtained with alkaline catalysts is generally not high and not washfast. Resin particles presumed to form within the fiber under these conditions may be hydrogen bonded to adjacent cellulose chains and thus act as cross-linkages as long as the fiber is dry. The lack of washfastness can perhaps be attributed to rupture of these bonds by water. Moreover, the possibility that such compounds as dimethylol urea can cross-link cellulose even under alkaline conditions should not be excluded.

It has also been reported that no evidence of reaction of cellulose with urea and melamine formaldehyde precondensates was found in the infrared spectra of treated cellulose films, while the spectra of films treated with epoxy reagents and with formaldehyde indicated ether formation [66]. The recovery of all four films was increased by the treatment, but those which showed no evidence of ether formation lost the improvement on washing. While other workers did find spectroscopic evidence of ether formation in cellulose treated with urea and melamine formaldehyde precondensates [142, 412], and fabrics treated commercially with these compounds do not lose wrinkle recovery on washing, it appears that it may be possible to improve the wrinkle recovery of cotton by means other than covalent cross-linkages.

The cross-link theory. The cross-link theory is supported by an impressive amount of evidence [256]. Treatment with compounds which give water-soluble materials when polymerized by themselves gives fabrics which do not lose their improved recovery upon prolonged laundering [748]. Cotton's recovery can be improved by treatment with compounds which are not resin formers [182, 318, 559]. Polymerization of ethyl acrylate in allylated cotton fibers improves recovery, but polymerization within untreated fibers, which cannot be cross-linked by the acrylate, does not produce an improvement [214, 715]. The treated fabrics are not soluble in cellulose

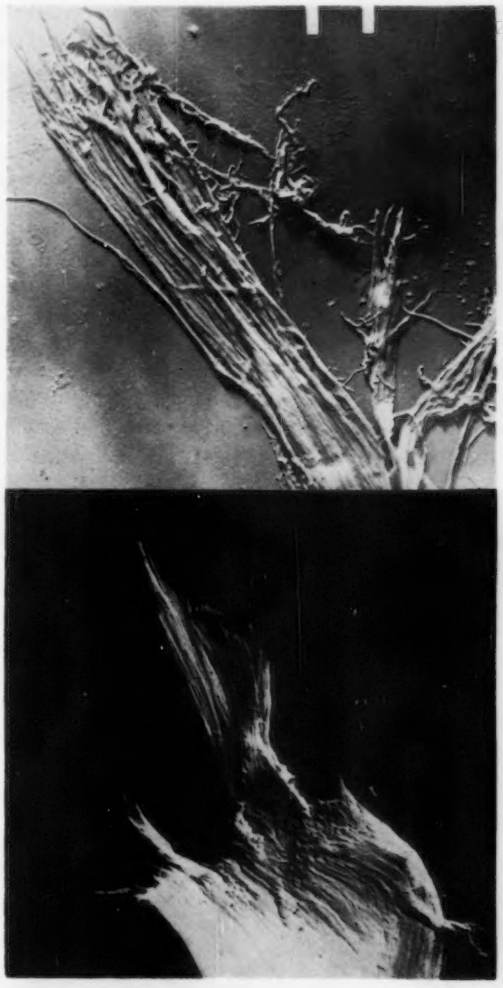

Fig. 8. Unlike cotton treated with monomethylol urea, which cannot cross-link cellulose, dimethylol urea-treated fibers do not disintegrate into thin sheets of microfibrils upon beating in water in a blender, but break into short, thick chunks of cellulose, several layers thick. Top: fragment of cotton treated to contain 10% monomethylol urea; bottom: fragment of cotton treated to contain 10% dimethylol urea.

solvents [567, 630], and they resist microbiological degradation, indicating that hydroxyl groups on cellulose chains in the treated fabrics are blocked [141, 276]. While insolubility in cellulose solvents and resistance to microbiological degradation can be obtained by means other than cross-linking [82, 609, 610, 611], these means are not effective on ultrathin sections of fibers investigated by electron microscopic techniques [599, 721]. Unlike cotton treated with monomethylol urea, which cannot cross-link cellulose, dimethylol urea-treated fibers do not disintegrate into thin sheets of microfibrils upon beating in water in a blender but break into short, thick chunks of cellulose several layers thick, suggesting the presence of both interfibril and interlayer cross-linkages (Figure 8). Cellulose treated with many creaseproofing agents has been found to exhibit an increased absorption in the 11 μ region, which indicates new ether groups and thus cross-linkages [142, 521, 675]. Furthermore, the absorption decreased rapidly upon acid hydrolysis, at a rate correlating with decrease in wrinkle recovery but faster than that for removal of the agents [412]. It may be surmised, on this basis, that it is the extent of bonding of the reagent with cellulose that is important in improving wrinkle recovery, not the mere presence of the reagent in the fiber. In view of the above, there is no doubt that cross-linking is at least sufficient, if not also necessary, for improving the deformation recovery of cotton.

Mechanism of improved recovery. Whether through resin-particle deposition or formation of covalently bound cross-linkages, or both, the improvement in recovery of cotton conferred by the treatments is believed to depend on a decrease in stress-induced slippage between the structural elements of the fiber. According to the proponents of the deposition theory, resin particles inside the fiber exert this effect mechanically, simply by being there. Fiber elements are entangled and their flow is hindered by the presence of rigid particles in interstitial spaces. The flow-hindering effect of these particles may be augmented by hydrogen bonding with hydroxyl groups on the cellulose chains. Also, since water cannot be adsorbed on resin-bonded hydroxyl groups, the resulting decrease in "internal lubrication" provides additional improvement in recovery [196]. According to the proponents of the cross-link theory, the decreased slippage is due to restraining action of covalent cross-linkages formed between structural elements of the fiber.

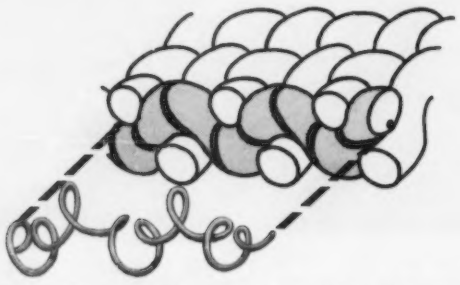

Fig. 9. Creaseproofing treatments stabilize the fibers in the configuration they had in the fabric during the curing step. Tortuous as it may be, this is the configuration to which they tend to return after stressing, and this is why the fabric acquires wrinkle resistance.

The first step in creaseproofing treatments consists in impregnating the fabric with a water solution of the reagents. The water breaks a number of hydrogen bonds between the structural elements of the fibers. This affords a measure of freedom, and permits them to rearrange and assume a configuration in which they are under the least strain. The fabric is then subjected to drying and curing, during which moisture is evaporated and new hydrogen bonds and covalent or hydrogen-bonded cross-linkages are formed between the fiber elements. These hinder fibrilar and molecular slippage and stabilize the fibers in the configuration they had in the fabric during the curing step (Figure 9). Tortuous as it may be, this is the configuration to which they tend to return after stressing, and this is why the fabric acquires wrinkle resistance.

It should be pointed out that the treatment need not necessarily be applied to flat fabrics. The improvement in deformation recovery obtained as a result of the treatment can be utilized, therefore, in a number of ways, of which improved wrinkle resistance is but one. For example, a cured-in crease is just as durable as a smooth surface, and the process can and is used to insert durable creases and pleats as well as to prevent wrinkling.

Level of Deformation Recovery

Maximum deformation recovery level. If the effect of the treatments depends on reduction in slippage between fiber structural elements, it follows that the improvement in deformation recovery obtained should be proportional to the number of cross-linkages. However, the relationship between extent

of cross-linking and improvement in recovery level is not a direct one. In general, for a given agent, the higher the treating bath concentration the larger the amount of the reagent that is bound to cotton and the higher the wrinkle resistance of the treated material. But once a certain recovery level is achieved, little further improvement can be obtained by applying additional quantities of the reagent.

In commercial practice this limit is seldom reached. Strength losses which accompany the treatments impose an earlier limit, based on the maximum strength loss allowable. Fabrics are not given the highest possible degree of wrinkle resistance because they would lose so much strength in the process that they would no longer be useful. There has been, therefore, comparatively little interest in determining the true maximum recovery levels attainable in cotton [235].

One possible reason for the apparent limit on cotton's wrinkle recovery is evident. The improvement in wrinkle resistance should be directly proportional not to the number of cross-linkages in the fiber but to the degree of restraint on slippage between the fiber elements given by the treatment. Accordingly, the first few cross-linkages should exert a greater effect per cross-link than those introduced subsequently, and the relationship between extent of cross-linking and wrinkle recovery should be logarithmic [226]. An upper limit in the improvement attainable by this method is also to be expected, since once an amount of the reagent sufficient to immobilize the fiber elements is introduced, additional cross-linkages cannot further improve the deformation recovery of the fiber. However, this does not explain why it is possible to obtain higher recovery levels with some compounds than with others.

Extent of cross-linking. While it is not difficult to understand why doubling the amount of reagent bound to cotton (the add-on) does not double the improvement attained, it would seem reasonable to expect that fibers cross-linked to the same extent would have the same deformation recovery. Yet, some creaseproofing compounds seem more efficient than others, even when the comparison is made on what may be termed "molar add-on," that is, on the basis of the number obtained by dividing the weight add-on by the molecular weight of the compound used.

Even when two different reagents are applied to fabrics in such a manner that in each case the molar add-on is the same, it does not necessarily follow that the extent of cross-linking in each fabric is also the same. The number of cross-linkages formed in the fibers is related to the concentration of the reagent in the bath and to the amount of the agent bound to cotton, but much also depends on chemical properties of the compound used and on reaction conditions. Some compounds, for example, may be less reactive with cellulose than others. These are more likely to form a larger number of side groups on the cellulose chains than the more reactive cross-linking compounds. Some compounds, those capable of polycondensation as well as cellulose cross-linking, may polymerize to some extent in the course of the reaction. These would form cross-linkages composed of a number of molecules, or polymeric side chains, or perhaps even resin particles not bound to cotton cellulose by primary valence bonds but still embedded in the fiber so that they are washfast. Reacting the compounds in swollen fibers may result in a higher ratio of intra- to intermolecular cross-linkages than dry cures.

The formation of polymeric cross-linkages and side chains may be favored by high concentrations of the reagent. For example, every time a diepoxide compound cross-links cotton cellulose, two hydroxyl groups are formed on the cross-link itself. If other molecules of the reagent are in the vicinity, they may react with these hydroxyls rather than cellulose hydroxyls, thus forming side chains on the cross-link.

High curing temperatures may cause some creaseproofing agents to decompose. The resulting fragments of the molecule may volatilize or form cross-linkages on their own if they are capable of it. This is rather likely in the case of the N-methylol compounds, since formaldehyde can split off fairly easily and it can form methylene cross-linkages.

A method for the precise determination of the number of cross-linkages in a treated fabric has not yet been devised, and it is impossible to establish the relationship between the extent of cross-linking and wrinkle recovery with certainty [710]. It has been suggested that, of the amount of reagent required for a given wrinkle recovery improvement, only a small fraction is involved in *inter*molecular cross-linking, indicating some kind of *intra*molecular bridging [520]. It appears that, while the degree

of improvement in wrinkle resistance of fabrics treated with creaseproofing compounds depends largely on extent of cross-linking, the structure and size of the cross-linkages, and their location within the fiber, are also important.

Structure and Size of Cross-Linkages

Long cross-linkages. A long cross-linkage is likely to be somewhat less effective than a short one in preventing chain and fibril slippage. Even if the ratio of length to distance spanned is more important than length of cross-link, short cross-linkages are more likely to be taut and effective than long ones. Formaldehyde, which forms the one-atom-long methylene cross-link, is in fact extremely effective, while resin precondensates, which may polymerize prior to cross-linking, are less efficient.

It has been suggested that if cellulose chains in the fiber were bridged by long molecules, the fiber would not lose much strength. The long cross-linkages would permit molecular slippage and hence better load distribution and higher elongation. This theory received considerable attention.

The experimental evidence is contradictory. According to some published data, the longer the molecules of cross-linking agents the lower the losses in strength for a given level of wrinkle recovery [254, 260, 668]. According to the work of others, strength loss due to creaseproofing is always directly proportional to the degree of recovery conferred by the treatment, regardless of the type of reagent used or the degree of cure [499, 652]. According to still other work, 4-atom and 7-atom cross-linking agents give fabrics whose properties are better than those of fabrics treated with a 3-atom compound, but increases in the length of the reagent above 4 atoms result in no additional gains [348, 687].

Of course, longer molecules do not necessarily result in longer cross-linkages. Reagent molecules may react with each other before they react with cellulose, the resulting dimer or trimer of a short molecule forming a long cross-link. There is no easy and accurate method for determining the length of a cross-linkage actually present in a sample of cotton cellulose. According to some reports, there are on the average two monomeric units in a methylol urea cross-linkage [680]; for methylol ethylene urea the average number is $1\frac{1}{2}$, indicating an equal number of single and double linkages [237]. According to other reports, the degree of polymerization of methylol ethylene urea varies from 2 to 5, the more highly acid reaction conditions giving the higher DP [463, 464]. Other cross-linking agents may well give linkages of different lengths.

Differences in tensile losses obtained with various finishes may relate to those characteristics of the reagents which have no bearing on the length of the cross-linkages they give, such as ability to buffer acids [235, 280]. A part of the tensile loss due to creaseproofing results from hydrolysis by acid catalysts. It has been reported that with cyclic ethylene urea formulations as much as one-half of the total tensile loss is due to factors other than the cross-linking [237], though this figure is unusually high. The hydrolytic damage is lower in the case of triazone- or melamine-treated cotton, apparently because the basic nitrogen atoms in these compounds act as buffers.

Reflection on the theoretical basis of the cross-linking theory indicates that, apart from damage attributable to treating materials and conditions, strength losses caused by creaseproofing treatments should be independent of length of cross-link and be proportional to the improvements in wrinkle recovery obtained. Cross-linkages loose enough to permit fiber elements to rearrange under stress and thus share the load cannot increase fiber elastic recovery. On the other hand, taut cross-linkages would restrict slippage and thus improve elastic recovery regardless of their actual length. However, there may exist an optimum tautness, length, structure, and location for cross-linkages, and linkages of this optimum type might give a maximum improvement in cotton's deformation recovery at a minimum strength loss.

Elastic cross-linkages. It has also been suggested that the elasticity of cross-linkages may have an effect on deformation recovery and strength of the treated material. A cross-link comprising rigid rings, for example, might impart greater rigidity to the fiber structure than a more flexible long-chain linkage. If the cross-links themselves were elastic, it would prevent the relative motion of the structural components of the fiber. Applied stress would be, therefore, nearly as well distributed as before the treatment, and the fiber would lose almost no extensibility and strength. At the same time, the elastic cross-links would pull the fiber elements back to their original position upon removal of external stress. On the basis of this reasoning, several at-

tempts have been made to improve cotton's deformation recovery with elastomers and other thermoplastic polymers [50, 308, 370, 400, 506, 515].

These attempts appear not to have been successful. Rubbery materials are too bulky to penetrate the fiber and for this reason cannot be effective. However, available information shows that it is possible to impregnate cellulosic fibers with monomers which normally polymerize to give rubbery substances, and to polymerize them substantially within the fibers. Fabrics treated in this manner have shown no improvement in wrinkle recovery unless the compounds used were so modified that they could cross-link cellulose. Even in such cases, however, the increase in fabric recovery obtained is by far not as high as that conferred by the common agents.

It is not likely that this method will lead to a process conferring good wrinkle recovery. The rubber type of elasticity is a phenomenon exhibited by an aggregate of molecules, not by a single one. It is doubtful that a cross-link formed inside a fiber could contain a number of molecules sufficiently large to make it behave like rubber.

Distribution of Cross-Linkages

Monomeric treating agents penetrate the fiber more or less completely, but they apparently do not enter into the crystalline lattice of the cellulose. The first is indicated by electron microscope photomicrographs of fiber surfaces and by evidence from metal reduction, dye staining, and radiographic experiments [202, 206, 436, 450, 451, 505, 608, 719, 722, 748]; the second is indicated by identical X-ray diffraction patterns given by treated and untreated fibers [142]. Accordingly, it appears that creaseproofing agents react with the less regularly arranged cellulose molecules between and on surfaces of crystallites. If the hypothesis of crystalline microfibrils is accepted, this means that the sites on which the agents react lie in the regions between fibrils and on fibril surfaces. This view is supported by thermodynamic calculations [522] and other data [19], which indicate that the dimensional changes on wetting and drying of cellulosic fibers are due essentially to separation of microfibrils, with very little swelling taking place within them. It has been reported, however, that such hydrogen bond-breaking substances as urea can penetrate into regions in the cotton fiber which are not accessible to water [256]. This opens up the possibility of developing treating formulations capable of introducing cross-linkages in fiber regions not cross-linked by the conventional aqueous systems.

Effect of size of reagent. Polymerized resin precondensates may become so large that they cannot penetrate the fibers; they therefore coat fiber surfaces [258, 381, 436, 453, 519]. However, the comparatively small molecules of formic acid colloids of methylol melamine [80, 81] penetrate the fiber partially. Fibers from fabrics treated with such materials contain nitrogenous materials in the outer regions, with the fiber centers left largely free of nitrogen. Evidently, these molecular aggregates are not so large that they cannot enter the fiber, but their penetration rate is lower than that of smaller reagents. This dependence of penetration rate on reagent size may offer a means for directed cross-linking of cotton.

Effect of degree of distention. It has been suggested that the location of reaction sites depends on fiber distention at the time of treatment [430, 573, 687]. In the conventional process the fabric is impregnated, dried, and cured. The reaction is believed to take place in the dried, collapsed fibers. During drying, the treating formulation is likely to be squeezed from those regions in the fiber which are characterized by a comparatively high order of molecular arrangement. Accordingly, cross-linkages are likely to form primarily in the highly disordered regions. In the so-called "wet" process, however, the impregnated fabrics are not cured at high temperatures, and the reaction takes place in distended fibers. In this case cross-links are believed to form in regions characterized by moderate lateral order, because cellulosic chains or microfibrils in the highly disordered regions are likely to be spread so far apart that molecules of the treating agent could not span the distance between them. Wet beating of wet-reacted fibers generally results in fibrilation [721].

It must be noted that the reagents can react with single cellulose molecules, particularly in the distended regions, and formation of side chains and *intra*molecular cross-linking is quite possible.

Creaseproofing treatments appear to stabilize fibers in the state in which they were treated. Fibers cross-linked when dry tend to maintain their collapsed, restricted state on wetting, and fibers reacted in the swollen state tend to maintain their distended structure even when dry. This is what may be expected

if the dry process cross-links the disordered regions, and the wet-cure process cross-links the regions of moderate order.

This view leads to the concept of dual function of cross-linkages. Linkages formed in the dry fiber in highly disordered regions have primarily a restrictive effect. They bind molecules and microfibrils together, hinder slippage between them, and lower the capacity of the fiber to swell, to absorb moisture, and to accept dye. Linkages formed in regions characterized by greater lateral order are likely to have a disruptive effect. Formed between two microfibrils spread apart by water, a cross-link prevents them from becoming contiguous to each other again on drying. Such cross-links therefore decrease the amount of hydrogen bonding in the dry fiber; increase the possibility of chain slippage; increase regain, swelling, and dye absorption; and make the fiber more accessible.

Side chains have a disruptive function regardless of location, but those in highly disorganized regions would not affect fiber properties as much as those in regions of higher lateral order. Of course, some *intra*molecular cross-links and side chains may be capable of forming hydrogen or polar bonds with hydroxyl groups on cellulose or with each other.

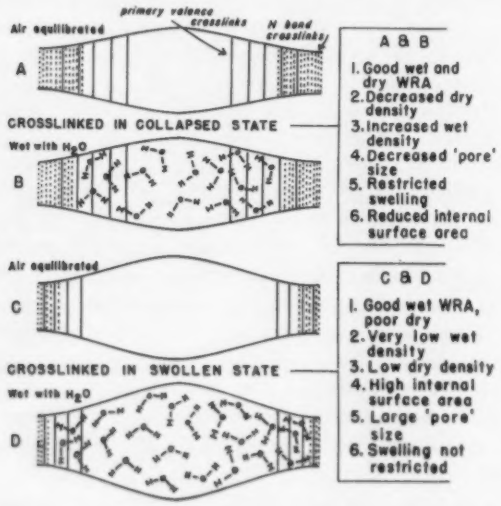

Fig. 10. In the dry-cure process (A and B) cross links are likely to form primarily in the highly disordered regions. They restrict swelling and impart good wet and dry wrinkle resistance. In the wet-reaction process (C and D) cellulose chains and microfibrils in the disordered regions are likely to be spread so far apart that reagent molecules cannot span the distance between them. Cross-links form mainly in regions characterized by moderate lateral order and therefore impose no restraint on chain and microfibril slippage in dry fibers, where it takes place primarily in highly disordered regions. However, they stabilize the swollen structures and restrain slippage when the fibers are wet.

Regain and drying characteristics. Conventional dry-cured cottons have a decreased, and wet-reacted cottons an increased, regain [398, 548, 682], but both are claimed to dry in a shorter time than their untreated counterparts [21, 673]. That fabrics whose fibers absorb less water dry faster than those that hold more is understandable enough. Whether the actual rate of drying is higher or not, they have less water to lose. It is conceivable that the wet-reacted cotton dries faster because cross-links or side chains in regions of some lateral order increase both absorption and desorption rates. Cotton treated with tributyl phosphate to give butyl ethers of cellulose has also been claimed to absorb water and to dry faster than untreated cotton [489]. The bulky substituents on the cellulosic chains may act in the manner of cross-linkages in the wet-reacted cotton.

Dry and Wet Wrinkle Resistance

The "natural" deformation recovery of cotton depends largely on "natural" hydrogen bonding between its structural elements. Heating, which removes moisture and increases hydrogen bonding, improves cotton's wrinkle recovery. However, only dry recovery is improved in this manner, since hydrogen bonds are susceptible to rupture by moisture. The dry-only recovery obtained by treatments with certain resin-forming compounds or such salts as borates [547], and that exhibited by cotton oxidized with periodic acid [420], may also be attributable to formation of water-sensitive bonds. Conventional methods, which introduce covalent cross-linkages into the fibers, improve both wet and dry recovery of the products. Recovery in the wet state is generally lower but, because cotton is nearly as accessible to cross-linking agents as it is to water, this difference is small [676].

Wet-only wrinkle recovery. Making cotton more accessible to moisture appears to improve its recovery in the wet but not in the dry state. For example, partial phosphonomethylation yields fabrics having a high wet wrinkle resistance; however, they are stiff and easily wrinkled when dry [329]. The wet recovery obtained may depend on internal pressure

generated by swelling forces, somewhat like the deformation recovery of a hose filled with water under pressure.

The internal pressure mechanism may also contribute to the improvement in recovery obtained by wet-reaction processes. The reaction takes place on swollen fibers, and side chain and *intra*molecular cross-linking is possible [520, 676]. However, the reagents used are difunctional and capable of cross-linking cellulose, and the presence of covalent cross-links in the products is indicated by their insolubility in cuprammonium, dimensional stability, and high recovery level attained at low add-ons [573, 599, 721]. It has been suggested that cross-linkages introduced by the wet-reaction process are located largely in regions of some lateral order; they therefore impose no restraint on chain and fibril slippage in dry fibers, in which slippage takes place primarily in highly disordered regions (Figure 10). However, these cross-links stabilize the swollen structure and restrain slippage when the fibers are wet.

The wet-only recovery obtained by reacting swollen cotton may also be interpreted in terms of taut and loose structures [431]. Cross-linkages introduced by this process limit chain and fibril mobility only as long as the fiber is distended and distances between its structural elements are high (Figure 11). When the fiber dries, there is no restraint on slippage, because the whole structure collapses and its elements become loose.

Optimum dry and wet wrinkle recovery. Cross-linking cotton at an intermediate state of distention (neither fully swollen nor completely collapsed) yields products with better properties for most normal uses than treatments at either extreme [126, 573]. Such fabrics have lower swelling capacity and lower wet recovery than those reacted swollen, but have the advantage of dry wrinkle resistance. Compared with dry-cured fabrics, they are more absorbent and have higher wet wrinkle resistance. High dry and wet wrinkle recovery can also be obtained by conventional resin treatment of fabrics previously reacted in the swollen state [572].

Finish Durability

The improved recovery from deformation imparted to cotton by treatment with polyfunctional cellulose-reactive compounds is durable. However, while some finishes cannot be removed at all under conditions in which the fabric itself does not disintegrate, others are affected by laundering, particularly by the high alkalinity and by the "souring" step employed by commercial laundries [662]. The degree of durability depends on treating agents used and reaction conditions.

Hydrogen and covalent bonds. Much has been said about the distinction between resin precondensates and so-called "reactants," which do not form cross-linked polymers by themselves and are believed to cross-link cotton cellulose through covalent bonds. Wrinkle recovery obtained with the earlier resin precondensates was found to be less durable to laundering than that obtained by treatment with the reactants, and it has been suggested that resin precondensates, as a class, are less durable. However, the finish given by diepoxide compounds, which can form insoluble polymers, resists both acid and alkaline hydrolysis, while the reactant agent, dimethylol ethylene urea, can be stripped from fabrics by comparatively mild acid solutions. The differences in the durability of the creaseproofing agents cannot, therefore, depend on their ability to form insoluble resins. As mentioned, the possibility of hydrogen bonding between the creaseproofing agent and the hydroxyl groups on cellulose cannot be excluded. Compounds which contain polar groups, such as the various urea derivatives with their carbonyl groups, are likely to form hydrogen bonds. Hydrogen bonds can be broken by water, and to the

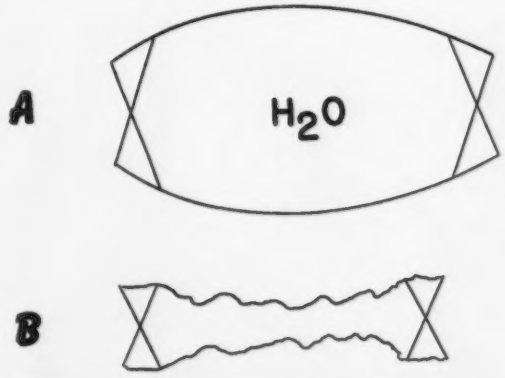

Fig. 11. Diagramatic representation of a wet-reacted fiber structure. A: Water-swollen, distended, exhibiting wrinkle recovery; B: dry, collapsed, exhibiting no wrinkle recovery.

extent that the effect of a reagent depends on hydrogen bonding, the improvement obtained may not be washfast. Cotton is more accessible to alkali solutions than to water [339], and the detrimental effect of strongly alkaline laundering may perhaps be ascribed, in part, to the larger number of hydrogen bonds broken by the alkaline solution.

The loss in wrinkle resistance exhibited by fabrics washed for the first time is usually higher than that exhibited after each subsequent washing. A part of the initial loss may perhaps be ascribed to rupture of the most highly strained cross-linkages and to a decrease in hydrogen bonding between the cellulosic chains and possibly between the treating agent and cellulose hydroxyls. Subsequent losses, however, are more likely to be caused by progressive hydrolysis of covalent cross-linkages.

The nature of the functional group. The reactive group in cellulose is the hydroxyl group, and the commercial cross-linking agents are chemically bound to cotton through an ether bond. The differences in their stabilities to hydrolysis must therefore be ascribed to the influence of atoms adjacent to the ether oxygen. Little has been published on the reasons why some cross-linkages are more susceptible to hydrolysis than others, though the relative stability of the various compounds has been established fairly well. The methylene cross-linkages formed by formaldehyde cannot be stripped from fabrics unless strong acid is used. Epoxides, chlorohydrin derivatives, and acetal reagents also give acid- and alkali-resistant finishes. Nitrogen-containing compounds exhibit less resistance to hydrolysis, but there are significant and so far unexplainable differences among the individual members of this family. The tris-1-aziridinyl phosphine oxide (APO) finish is quite stable. Triazine and triazone compounds are less durable, but they are superior to the methylol ureas.

In general, the -C-CH_2-O-Cell linkages are more resistant than those formed by the N-methylol compounds, particularly those of the amide (-CO-NH-CH_2-O-Cell) type. The greater susceptibility to hydrolysis of N-methylol compounds suggests that the presence of the basic nitrogen atom beta to the ether oxygen plays a role in the reaction. The hydrolysis may be initiated by addition of a hydrogen ion to this nitrogen. If so, substituents making the nitrogen atom less basic would improve the finish durability. However, since both cross-linking and hydrolysis proceed through acid-catalyzed mechanisms, such substituents on the nitrogen atom, while they may render the cross-linkages more durable, would also render the compound less reactive. Compounds which give stable cross-linkages, as for example compounds in which the atom beta to the ether oxygen is a carbon atom, are in fact much less reactive than the N-methylol compounds.

The constitution of the reagent. Loss in wrinkle recovery may result from hydrolysis of the bond between the treating agent and cellulose, but it may also be due to hydrolysis within the cross-link itself. For example, it has been pointed out that wrinkle resistance obtained by treatment with diepoxides may not be washfast if the fabric is treated with a compound in which the chain linking the two epoxide groups contains an easily hydrolyzable bond [263].

It has also been pointed out that if polymeric cross-linkages are formed during the treatment the bond between two molecules of the reagent may be more susceptible to hydrolysis than the bond between the reagent and cellulose. Thus, the >N-CH_2-O-CH_2-N< linkage, which could form between two molecules of dimethylol ethylene urea, is more likely to hydrolyze than the >N-CH_2-O-Cell linkage.

The molecules of the creaseproofing agents may also exert a protective effect. For example, the higher acid resistance of triazones and triazines, as compared with urea and cyclic urea compounds, may be due to the presence of an acid-buffering tertiary nitrogen atom in their structures.

Treating conditions. Finish durability depends on constitution and chemical properties of the treating compounds, but reaction conditions have a marked influence on results obtained. "Hard" cures improve the durability of the finish, though the initial wrinkle resistance level may not be much higher than that given by "soft" or by room temperature cures. Hard cures use strong catalysts and high curing temperatures, and are therefore presumed to result in more complete reaction. The high initial wrinkle-resistance level of fabrics given the soft cure may be due to hydrogen bonding. In the case of N-methylol compounds, hard cures may also transform the theoretically possible >N-CH_2-O-CH_2-N< linkage, which would be comparatively unstable, to the more stable >N-CH_2-N< linkage; the released formaldehyde may form stable methylene cross-linkages.

Strength Losses

Cotton fabrics exhibit strength loss after creaseproofing treatments. A part of this loss can perhaps be ascribed to acid damage. However, it is likely that the same changes in the structure of the cotton fiber which lead to higher deformation recovery and wrinkle resistance also cause a decrease in fabric tensile and tear strengths and abrasion resistance.

Tensile losses. The highest strength is attained in a fiber when the flexibility of its structure is high enough to permit full distribution of load and yet not so high that failure can occur by slippage of the structural elements past each other. In cotton, applied load is not fully distributed among structural elements of the fiber. Failure appears to occur by consecutive breaking of those structural elements that carry the brunt of the load; it propagates through the fiber by passing from one area of stress concentration to another. When the cotton fiber is cross-linked, the flexibility of its structural components is decreased. Consequently, the degree of load distribution possible is also diminished, and the treated fiber fails at lower loads. Fabric tensile strength reflects the tensile strength of its component fibers.

Fibers cross-linked in the collapsed state are not penetrated by moisture to the same extent as untreated fibers, and wetting does not increase flexibility of their structural elements, and consequently their strength, as much. For example, the difference between oven-dry strength and the strength at 60% RH, which amounted to 11.8 lb. for an untreated cotton fabric, was only 4.2 lb. for the same fabric after conventional creaseproofing [652]. The moisture-absorption capacity of fibers cross-linked in the distended state is increased by the treatment. Their strength at normal humidity levels is not affected by the treatment as much as that of dry-cured fibers; however, their wet strength is affected more [587].

It should be noted that it is possible to decrease tensile losses and even to increase the tensile strength of cotton fabrics by applying tension during the treatment [316, 317, 523, 526, 723]. In this case the cross-linkages improve load distribution because they form in the fiber subsequent to the alignment of its elements under stress.

Tear strength losses. The decreased mobility of cross-linked structural elements decreases fiber extensibility. Tear-strength losses exhibited by the treated fabrics may be due to this factor, though it has also been suggested that the finishes increase friction between threads, and the resulting higher resistance to slippage is responsible for tear strength reduction [295, 306, 671, 681]. There is a striking analogy between the mechanisms responsible for tensile and tear strength losses. In both the cause is the decreased ability of the structure to distribute an external load among a large number of its elements. Tensile loss results from poor load distribution among structural elements of the fiber. Tear-strength loss results from a decrease in the ability of yarns to share the applied load. In a fabric, as a tear progresses, new yarns come under stress. When fiber elongation and interfiber slippage are lowered, fewer yarns can accumulate at the point of tear propagation, and less force is required for the tear to continue.

Fibers cross-linked under tension have low extensibility, and while tension during treatment improves fabric tensile strength, tear strength may suffer additional losses. On the other hand, lubricating agents, which increase the ability of fibers and yarns to rearrange under load and share stresses, improve the tear but may lower the tensile strength of fabrics.

Losses in abrasion resistance. Reduction of fiber extensibility may also be responsible for the lower abrasion resistance of treated fabrics shown by laboratory tests [139, 260, 507, 691]. Abrasion losses seem directly proportional to extensibility losses. However, it has been found that as the load used in testing decreases, the difference between a treated and an untreated fabric diminishes, until at some point (i.e., under a certain load) they are on the same level; at very low loads it takes the machine longer to rub a hole through a treated fabric than an untreated one.

The explanation seems to be that fabric resistance to abrasion is affected not only by fiber extensibility but also by elastic recovery. At large loads, efficient distribution of stress among many fibers has primary importance. The reduced extensibility of treated fibers prevents good stress distribution, and such fabrics fail faster. At low loads, the increased elastic recovery of treated fibers becomes significant, and treated fabrics last longer than untreated ones. Since in normal wear garment stresses are low, and since at low loads the loss of extensibility is compensated for by an increase in elastic recovery, the results of common laboratory abrasion tests are not dependable indicators of actual wear life of a garment.

Addition of rubber latices or other thermoplastic materials to creaseproofing formulations has been found to improve wear properties of treated fabrics [3, 32, 71, 265, 486, 631].

Action of External Agents

Creaseproofing formulations generally include softeners or lubricating agents. The application of softeners in cotton finishing is, of course, not new. They have been used for years to modify fabric hand, to improve drape, etc. However, the use of these compounds to affect creasing properties of fabrics and to compensate for undesirable side effects of the treatments is pertinent to this study [297].

The lubricating mechanism. Softeners do not penetrate inside the cotton fiber. Their effect on wrinkle recovery must therefore be based on mechanisms superimposed on but distinct and different from those operating within the fiber. There is little doubt as to the mode of action of the long-chain, fatty softeners such as sulfated oils. Molecules of these compounds attach themselves to the surfaces of fibers, where they are held by polar bonds. Stearamide-containing formulations can be made to form primary valence bonds with cotton by treatment with formaldehyde. The fatty residues of the attached molecules lubricate the surfaces; cotton fibers on which such molecules are adsorbed exhibit a decrease in interfiber friction. This makes for higher fiber mobility and increases the degree to which an applied stress can be shared. Better distribution of applied stress, in turn, leads to lower deformation of individual fibers and higher deformation recovery. The increased lubricity also favors higher recovery because the external friction which the recovering fibers must overcome is diminished.

Softeners based on silicone compounds also act as lubricants [140, 421, 471, 644, 758]. Many contain blends or copolymers of dimethyl and methylpolysiloxane. The former provides lubrication through its many methyl groups, while the latter cross-links and contributes durability.

The elastic bridge mechanism. Polyethylenes [32, 185, 585, 601], acrylics [3, 220, 517, 678, 693], and other thermoplastic polymers [219, 265, 475, 641] are also used as softeners for creaseproofed cottons, but the mode of their action is less clear. Two mechanisms, acting separately or jointly, have been suggested [142, 224, 624, 678]. The first is the usual lubricant mechanism, which depends on decreasing friction between yarns and fibers. The second depends on formation of elastic bridges between yarns and possibly between fibers. According to this concept, these elastic bridges act somewhat like rubber bands. Their modulus is low, and they extend easily even under low stresses, so that rearrangement of yarns under stress is not significantly hindered. Applied stress can thus be shared almost as well as in their absence. When the stress is removed, the yarns are actually pulled back together by the stretched elastic bands. This theory bears a resemblance to the elastic cross-link theory discussed earlier. However, the yarn-to-yarn or fiber-to-fiber elastic bridges are not as limited in size as bonds that can be formed in interstitial spaces inside the fiber. The elastic bridge mechanism may be responsible for increase in wrinkle recovery, where the strains involved are comparatively small. The friction-reduction mechanism may provide for changes in tear and tensile strengths, where the strains involved are so high that the bridges would have to be broken. According to these theories, softeners which act primarily as lubricants should be best suited for tightly woven fabrics, and the rubbery thermoplastics should be superior for loose constructions.

Improvement in Cotton's Wrinkle and Deformation Recovery: Materials

The literature on materials used in improving cotton's wrinkle recovery is voluminous. Each of the major types of chemical agents has been described in considerable detail, its advantages and disadvantages pointed out and compared with those of other compounds. Many reviews have also been published [8, 91, 94, 147, 157, 175, 176, 177, 178, 193, 203, 205, 289, 290, 298, 363, 367, 411, 426, 438, 439, 442, 460, 508, 510, 536, 579, 580, 605, 649, 653, 655, 664, 750, 751, 752, 780]. In addition technical data on the various proprietory formulations can be obtained from chemical manufacturers. In view of the availability of information, this section of the study contains a minimum of descriptive material. An effort is made, instead, to correlate the constitution and chemical properties of the compounds used with their mode of action and physical and chemical properties of the finished fabrics. Fabric susceptibility to damage on bleaching with sodium hypochlorite, odor formation, and lightfastness to dyes, which depend

largely on the chemical nature of the materials employed in the treatment, are also discussed.

Formulations used in improving cotton's wrinkle recovery generally comprise creaseproofing agents, catalysts, and such auxiliary compounds as softeners, hand modifiers, optical brighteners, and wetting agents [4, 65, 69, 71, 79, 108, 148, 222, 249, 262, 297, 409, 456, 475, 494, 497, 526, 528, 590, 602, 684, 689, 701, 707, 736, 789]. Dyes may also be included [163 371]. Blends of various agents are often used to take advantage of their synergistic properties. Several methods of identifying the various finishes used have been described [7, 13, 267, 273, 337, 386, 452, 480, 504, 533, 647, 703, 733].

Many compounds which confer wrinkle recovery on cotton are resin precondensates, and the term "resin treatment" is often used in the industry to denote treatments for making cotton wrinkle resistant. However, it is not the ability to polymerize or condense and form resins, but the ability to react with at least two hydroxyl groups on cotton cellulose that characterizes all creaseproofing agents.

Formaldehyde and other aldehydes. Formaldehyde, CH_2O, was the first material used to cross-link cellulose [209]. It can be applied to cotton both by the conventional and by the "wet-reaction" process. As might be expected, the first gives wet and dry wrinkle resistance, while the wet process gives wet-only wrinkle recovery.

Formaldehyde reacts with cotton cellulose in nonaqueous media sluggishly, if at all, and it has been suggested that in the presence of water its reactive form is methylene glycol [573]. The reaction must be catalyzed by comparatively strong acids. Methylene cross-linkages formed by formaldehyde are stable to both acid and alkaline hydrolysis.

Formaldehyde is not used in conventional cotton creaseproofing in spite of many papers [170, 213, 275, 286, 372, 430, 596, 597, 675, 687, 740, 787, 788] and patents [74, 79, 98, 183, 190, 316, 317, 538, 550, 617, 667, 768, 786] on such treatments. Volatile and irritating, it is difficult to apply. The greatest deterrent to the commercial use of formaldehyde in the dry-cure process, however, is the high strength loss exhibited by the treated fabrics. As indicated earlier, it has not been resolved whether this loss is due to the short length of the methylene linkage formed by formaldehyde or to such other factors in the process as nonuniform reaction or acid catalysts.

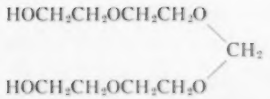

Fig. 12. The polymeric acetals, products of a reaction between aldehydes and polyalcohols, are said to cross-link cellulose by transacetalization with cellulose hydroxyls.

The use of formaldehyde in the wet reaction process was described in 1940 [97, 482, 483]. About twenty years later, interest was again expressed in this method [126, 292, 430, 572, 573]. Cotton fabrics given a mild wet treatment with formaldehyde exhibit but slight tensile losses. The fabrics can then be subjected to the dry-cure treatment, using comparatively small amounts of conventional reagents. The products exhibit good wet and dry wrinkle resistance at acceptable total tensile losses.

Several compounds said to release formaldehyde at a controllable rate have been proposed for use in cotton creaseproofing, but have not found commercial acceptance [75, 76, 77, 745].

The simplest dialdehyde, glyoxal, as well as other dialdehydes, have also been used for cross-linking of cellulose fibers [74, 78, 100, 535, 633, 635, 718]. Glyoxal is not as volatile as formaldehyde, but discoloration and strength losses are difficult to prevent, and it is not in wide use. It is tetrafunctional, and study of the reaction of this reagent with cotton indicates that it does in fact form all the theoretically possible linkages [310]. The hemiacetal bonds are not stable, but the acetals resist both acid and alkaline hydrolysis. Each aldehyde group can form a methylene cross-linkage, and the effect of treatment with glyoxal and other aldehydes is similar to that produced with formaldehyde.

Acetals. The polymeric acetals (Figure 12), products of a reaction between aldehydes and polyalcohols, are said to cross-link cellulose by transacetalization with cellulose hydroxyls [1, 353, 389, 390, 391, 392, 394, 395, 396, 552]. The finish is stable to both acid and alkaline hydrolysis. Acetals are often blended with *N*-methylol compounds [239, 352, 354].

Methylol urea compounds. Methylol urea compounds (Figure 13), products of reaction between urea and formaldehyde, were the first resin precondensates used commercially for improving cotton's wrinkle resistance [230]. These compounds are believed to react with hydroxyls on cellulose through their *N*-methylol groups, though resin formation may

also take place. Some polymerization is in fact quite likely to occur, both inside and on the surfaces of fibers. Surface resin gives the fabric a somewhat stiffer hand. The public associates wrinkle resistance with a crisp, full hand, and to some extent and in some applications this effect is desirable [437]. However, if the degree of surface resin formation is not closely controlled it may lead to a boardy hand and a "dusty" finish.

Methylol ureas, like other N-methylol compounds, react readily with cotton cellulose. The catalytic agents and the conditions required for the reaction need not be severe, and the reaction is easily controlled. The bonds between cellulose and the urea compounds, however, are rather easily hydrolyzed.

Efficiency of urea-formaldehyde (UF) precondensates as creaseproofing agents depends largely on the urea-formaldehyde ratio [299, 650]. Some commercial urea-formaldehyde agents are mixtures of dimethylol and monomethylol urea. The reaction product of urea and formaldehyde in the stoichiometric ratio of 1:2 is unstable in storage and imparts a strong formaldehyde odor to fabrics. Mixtures composed predominantly of monomethylol urea, which is monofunctional to cellulose, are inefficient creaseproofing agents.

Many formulations based on urea-formaldehyde, modified UF, and blends with UF have been proposed for imparting wrinkle recovery to cotton [71, 76, 79, 87, 88, 131, 132, 135, 185, 186, 195, 204, 210, 212, 236, 254, 303, 319, 350, 377, 384, 393, 415, 422, 503, 554, 639, 706, 772].

Cyclic methylol urea compounds. Cyclic methylol urea compound are tetrasubstituted derivatives of urea in which the two nitrogen atoms are connected by a carbon chain [237, 433, 439]. The most widely used of these compounds is the efficient dimethylol ethylene urea, or 1,3-bis-(hydroxymethyl) -2-imidazolidone (DMEU) (Figure 14) [590, 732]. Fabrics treated with DMEU can be given high wrinkle-resistance levels at low add-ons and without excessive strength losses. DMEU does not form an insoluble resin; it is stable in storage and in the treating bath, and because it does not form surface resin it does not affect the hand of the fabrics. DMEU reacts with cellulose readily, but the finish is susceptible to acid hydrolysis.

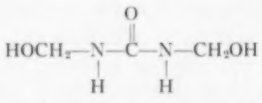

Fig. 13. Methylol urea compounds, products of reaction between urea and formaldehyde, were the first resin precondensates used commercially for creaseproofing cotton.

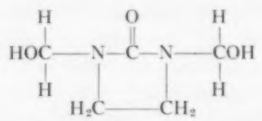

Fig. 14. Dimethylol ethylene urea (DMEU), or 1,3-bis-(hydroxymethyl)-2-imidazolidone, is a widely used cyclic methylol urea creaseproofing agent.

Several compounds related to DMEU [61, 238, 250, 253, 278, 284, 325, 347, 383, 449, 574, 717, 730, 792, 793, 794] and blends of DMEU with other agents [205, 239, 545, 665, 689, 756, 761, 783, 785] have been proposed for creaseproofing cotton.

Triazones. The triazone compounds (e.g., 1,3-dimethylol-5-hydroxy ethylperhydrotriazone-2; Figure 15) possess the closed ring structure of cyclic methylol ureas, but the chain connecting the two amide nitrogens contains a tertiary nitrogen atom. The method of preparation and the use of triazones for imparting crease resistance and dimensional stability to cellulosic materials were disclosed in 1943 [112], but they did not come into commercial use until about 10 years later. Their main drawbacks were listed as low efficiency, discoloration at the high temperatures used in commercial curing, and susceptibility to odor formation. Several different triazones have been synthesized [727]. Present commercial triazone formulations often comprise other creaseproofing agents and are said to have improved properties [236, 271, 345, 577, 760]. Triazones, like DMEU, do not form cross-linked resins, but because of a higher molecular weight are less efficient. However, they are less susceptible to chlorine damage and acid hydrolysis, possibly because of the tertiary nitrogen in the molecule.

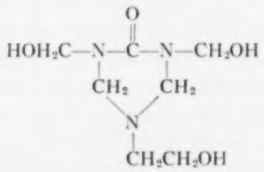

Fig. 15. The triazone reagents, such as the 1,3-dimethylol-5-hydroxyethyl-perhydrotriazone-2, possess the closed ring structure of cyclic methylol ureas, but the chain connecting the two amide nitrogens contains a tertiary nitrogen atom.

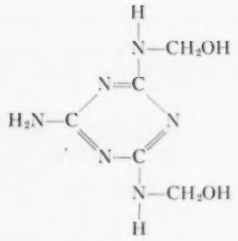

Fig. 16. Dimethylol melamine is one of the triazine creaseproofing agents based on formaldehyde-melamine reaction products.

Methylol melamine compounds and triazines. Methylol melamines (Figure 16), or triazines are prepared by reacting melamine with formaldehyde. By varying the ratio of reagents one may vary the degree of substitution—the number of methylol groups in the final product [378]. Subsequent methylation and other modifications produce improved materials [88, 132, 133, 146, 220, 285, 344, 374, 418, 461, 484, 557, 638, 690, 696, 729, 731, 774, 785].

Methylol melamines are comparatively large molecules, and they are capable of resin formation. Their efficiency, on a weight basis, is not as high as that of cyclic ureas, but they produce comparable wrinkle recoveries at lower strength losses. They also give a more durable finish, possibly because of the tertiary nitrogen atoms present in their molecules.

Many formulations employing blends of melamines or modified melamines with other compounds have been disclosed [80, 81, 205, 208, 254, 344, 545, 639, 665, 706, 761, 783, 785].

Epoxides and related compounds. The epoxide compounds used in improving cotton's wrinkle resistance are characterized by the presence of two epoxy groups (Figure 17) and are used in combination with other agents [136, 137, 208, 261, 263, 298, 435, 481, 490, 631, 632, 635, 697, 713]. Like the other resin precondensates, epoxy reagents are capable of polymerization as well as cellulose cross-linking. In creaseproofing, the cross-linking reaction is believed to dominate because the ratio of epoxy groups to cellulose hydroxyls is low, but the mechanism of the epoxide–cellulose reaction is not yet quite clear [411, 462, 479, 634]. The finish given by the epoxide compounds is stable to both alkaline and acid hydrolysis.

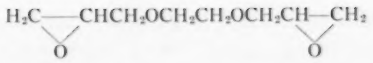

Fig. 17. The epoxide compounds used in creaseproofing cotton, such as diglycidyl ether of ethylene glycol, are characterized by two epoxy groups.

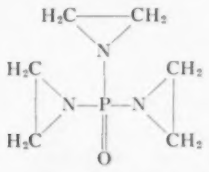

Fig. 18. Tris-1-aziridinyl phosphine oxide (APO) imparts both crease and flame resistance to cotton.

Polymerization or side chain formation may be partly responsible for the low efficiency of the epoxide reagents. However, their high molecular weight bears the major responsibility for it. Low molecular weight diepoxy compounds, such as butadiene dioxide, have been found effective as cross-linkers of cotton cellulose. However, many of them are volatile or toxic, and therefore inefficient and not easily adaptable for use in textile finishing plants.

Epichlorohydrin, which is used in preparing epoxy reagents and related compounds such as the dichloropropanols, have been found suitable for cross-linking cellulosic fibers [104, 179, 182, 247, 410, 488].

Multipurpose finishes. Some of the reagents which improve cotton's wrinkle recovery also impart other desirable properties. A process for simultaneous crease- and flameproofing, which employs methylol melamine, methylol dicyandiamide, and acids of phosphorous, was patented in 1952 [115]. Another patent discloses the use of an ester of phosphoric acid in which at least two of the acid groups are esterified with alcohols having an epoxy group [487]. Tetrakis (hydroxymethyl) phosphonium chloride (THPC) and tris-1-aziridinyl phosphine oxide (APO) (Figure 18) also impart crease and flame resistance [123, 180, 181, 566, 568, 569, 570].

APO can cross-link cellulose through ether linkages formed by opening the aziridinyl ring, but it is also capable of polymer formation. The durability of the APO finish to laundering is unusually good for a nitrogenous compound.

Other creaseproofing agents. With the exception of multipurpose finishes and formaldehyde, the fore-

going discussion had been limited to commercial creaseproofing agents and closely related compounds. These, however, by far do not exhaust the list. Among other compounds proposed for use as creaseproofing agents are condensation products of formaldehyde with acetone [165, 248, 249, 474], with acrolein [251, 252], with acetone and acrolein [790], with phenol [124, 184, 231, 232, 476], with diethylene glycol dicarbamate [598], with formamide [728], with hydroxyl amines [111, 217], with polymerized methacryl amides [692], with urea and alkylene oxides and epichlorohydrin [797, 798], with tetrahydro-iminopyrimidine [73], with hydrazides of mono- and dicarboxylic acids [174, 331, 332, 712], with low-molecular-weight polyesters or polyurethan [407], with nitrilotripropionamide [694], with glyoxal and urea [105], with hexamethylene diamine and urea [186], with hexose ureides [465], with dicyandiamide and urea [90, 195], and with 2-oxo-4,5-diimino parabanic acid resins [747]; the urons [369]; chloromethyl ethers of polyhydric alcohols [616]; dicarboxylic acid anhydrides and diesters [161, 318]; copolymers of ethylenic dicarboxylic acids with vinyl compounds [201]; salts of poly (vinyloxyalkyl) amines [108]; cyclopropyl quaternary ammonium compounds [358]; silicones and resin precondensates [444, 716]; quaternary ammonium derivatives of silicones [359], and halosilanes [593, 594]; bis (hydroxymethylurethan) of 1,4-butanediol [606]; orthophosphoric acid, urea, and sodium hydroxide [55]; diisocyanates [304]; aldehyde-ethylene imine reaction products [125] and phosgene-ethylene imine reaction products [127]; formyl alkyl oxetanes [473]; divinyl sulfone [628], its derivatives [711], and vinyl sulfone-urea addition products [618]; onium compounds [558, 559, 560]; and rubber latex with chloromethyl ethers [380].

There is little doubt that other creaseproofing agents will be disclosed in the near future [228].

Catalysts

The reaction between the various creaseproofing agents and cotton cellulose will take place simply on heating the impregnated fabric, but the length of time required for the reaction and the low durability of wrinkle resistance obtained in this manner make it necessary to use compounds which accelerate the reaction and stabilize the finish. Because their primary function is to increase the rate of the reaction, these compounds are commonly referred to as catalysts. However, they are often used in amounts which indicate that their function is not merely catalytic.

Cotton can be cross-linked by reaction with compounds which have double bonds, like divinyl sulfone [628]. Such reactions are catalyzed by alkalies. The chlorohydrin compounds used in some wet-reaction processes and the onium compounds are also applied in an alkaline medium [558, 559, 560]. The use of basic catalysts in creaseproofing formulations containing N-methylol compounds has not proved successful commercially [118, 207, 257]. Commercial catalysts now used are all acidic or acid-liberating compounds, and it is generally thought that their function is to provide the acidity presumed to be necessary for the cross-linking reaction. However, there is some evidence that the metal salt catalysts enter the reaction through a complex with the nitrogenous reagents [795].

Cellulose is hydrolyzed by mineral acids and by strong organic acids, and these compounds are not, therefore, used as catalysts except in special cases [96, 292, 614, 732, 767, 768]. Moreover, even weak acids promote premature reaction in the treating bath. Simple acid catalysts have been replaced almost completely by so-called "latent" acid catalysts, which are comparatively stable in the bath but release or form acids at the high temperatures of cure [109, 360]. Ammonium salts [11, 70, 74, 253, 622, 705], amine salts [190, 288, 323, 498, 500, 502, 637, 714], and metal salts [129, 144, 145, 355, 613, 698] belong to this category.

It has been suggested that carboxyl groups present in carboxymethylated cotton could serve as local catalysts [167, 168, 379, 586]. However, this method is not used commercially. The epoxy group is less reactive than the methylol group, and the epoxides require strong catalysts, such as zinc fluoroborate or magnesium perchlorate [435, 634, 713].

Each of the various catalysts used has certain practical advantages and disadvantages in reaction rates, odor formation, susceptibility to damage by chlorine, damage to fabric, etc. [59, 255, 281, 322, 429, 607, 714].

Side Effects

Chlorine damage. Some wrinkle-resistant cotton fabrics are susceptible to the so-called chlorine damage [6, 10, 14, 53, 54, 93, 117, 128, 158, 205,

216, 245, 279, 364, 385, 511, 513, 537, 607, 619, 620, 621, 648, 683, 746, 749]. When fabrics creaseproofed with compounds containing hydrogen-bearing nitrogen atoms are bleached with hypochlorites, chloramine or chloramide compounds can form by substitution of chlorine on the nitrogen. These compounds are thermally unstable. On application of heat, as in ironing, they disintegrate, and hydrochloric acid is formed in the fabric, possibly through a free-radical mechanism [759, 795]. The damage is due to acid hydrolysis and possibly to oxidation of cotton cellulose. The extent of damage is modified by the buffering power of the cross-linking agent, augmented, if such metal salts as magnesium chloride or zinc nitrate have been used as catalysts, by the buffering power of the basic metal residue left in the fabric.

The cross-linking agent may be capable of neutralizing acids if it contains an amine group or a basic tertiary atom, but the presence of primary or secondary amines is undesirable because of the possibility of chloramide formation. A tertiary nitrogen, such as that present in triazines and triazones, protects fabrics from hydrolysis. When the tertiary nitrogen atom is a part of the conjugated ring, however, the fabrics may yellow. Metal-salt catalysts seem to inhibit this reaction. The mechanism involved is not known. APO-treated fabrics show no tensile damage, but they discolor on chlorination and ironing.

Metal catalysts are converted to the hydroxide or carbonate form by the end of the cure, and as such can neutralize acids. An alkaline afterwash increases the protective action of the catalysts by insuring conversion to the hydroxide form. The protection offered by metal salts is not permanent, however. The metal-containing residue is converted to a soluble salt in the course of the neutralizing reaction and is removed progressively by laundering.

Dimethylol cyclic urea compounds do not contain the chloramide-forming >NH group. As would be expected, fabrics treated with these compounds do not exhibit chlorine damage in home laundering [584]. However, after storage under humid conditions, and under commercial laundering conditions, which involve high temperatures, high alkali concentrations, hydrolyzing acid sours, and bleach concentrations often in excess of those recommended, chlorine damage may occur [59, 237, 455, 464, 485, 654, 757]. This damage has been ascribed to a "loosening up" of the finish (i.e., partial hydrolysis and degradation of the cross-linkages), which results in freeing nitrogen atoms capable of chloramide formation. However, the amount of chlorine retained even under these conditions is comparatively low. Fabrics treated with triazones, which contain the buffering tertiary nitrogen atom, generally show little chlorine damage.

Fabrics treated with compounds not containing nitrogen, such as the epoxides and acetals, do not retain chlorine at all and exhibit no chlorine damage. These compounds, however, are generally more expensive and less efficient, and find use primarily in blends with the cheaper and more efficient nitrogenous compounds. Some of the blends seem to have synergistic properties, but they still reflect the properties of their components [239].

Of course, fabrics cross-linked with >NH-containing compounds can be safely bleached with persulfates, perborates, or peroxides. Antichlor reducing agents, which break down the chloramines and remove the retained chlorine, may also be used to prevent chlorine damage [5, 233, 334, 365, 537].

Odor formation. Many formulations used for imparting wrinkle resistance to cotton contain free formaldehyde and its reaction products. Formaldehyde is volatile and irritating. Even though it is not used alone, enough is liberated from its reaction products during impregnating, drying, and curing to require special ventilation systems [18, 26, 422].

Formaldehyde liberation may continue even after cure, especially if fabrics are not afterwashed, and the chemical can accumulate in rooms in which large quantities of treated goods are stored. This is particularly true of air-conditioned rooms, where the same air is recirculated [39, 448].

Formaldehyde may be present in the fabric as a part of a larger cross-linking molecule, combined with the cellulose by itself, or adsorbed on the cellulose [326, 327, 335, 382]. Methylene cross-linkages, being exceptionally stable, are not likely to contribute to odor formation, but the adsorbed formaldehyde is easily liberated by heat and moisture. Formaldehyde can also be released by hydrolysis of cross-linkages of which it is a part [199]. Its evolution from finished goods decreases as its percentage in the treating formulation decreases, and metal-salt-catalyzed systems evolve less formaldehyde than those cured with amine hydrochloride

catalysts [58, 699]. Higher cure temperatures also lower formaldehyde evolution [531, 735].

The composition of a formulation, choice of catalyst, etc. are governed by many considerations, and the formaldehyde odor problem is only one of them. With the urea-formaldehyde resin precondensates, for instance, the higher the ratio of formaldehyde to urea the lower the chlorine retention, so that here the two requirements are in opposition. Aftertreatments with such formaldehyde acceptors as urea [603] or with bisulfites and ammonia [423, 738, 739] have been patented for prevention of odor, but unreacted amines in the fabric may lead to chlorine retention. A thorough, neutralizing afterwash will go a long way towards diminishing odor evolution from fabrics [294, 576]. Difficulties in storing rooms and garment manufacturing plants can be diminished by installation of special absorbing filters in air-conditioning systems. A method for masking unpleasant odors by perfuming fabrics has been disclosed [527].

An amine odor is occasionally encountered with cotton treated for wrinkle resistance [9, 28, 443]. It endangers sales because of its unpleasant fish-like quality. The compounds responsible for the fish odor are alkylamines, with trimethylamine [$N(CH_3)_3$] believed to be the chief culprit. This compound may be formed from ammonia and formaldehyde or methyl alcohol, possibly through formation of intermediate compounds [221]. Presence of formic acid results in increased odor formation [516]. Alkylamines are used in the production of triazones, and fabrics treated with commercial preparations of these materials are particularly susceptible to odor development. Thermal degradation of cross-linking compounds during cure can also lead to formation of alkylamines.

Some of the metal salt catalysts are believed to depress amine odor formation. In an acid medium, trimethylamine forms a stable salt, and the catalysts may simply provide the acidity necessary for salt formation. However, it has been found that some strongly acid catalysts do not hold methylamine in fabrics, while compounds which are less acid hold it tenaciously.

Use of large amounts of acidic catalysts to prevent evolution of methylamines is not recommended. Excessive acidity leads to hydrolysis of the finish and increases susceptibility to chlorine damage. Moreover, protection by catalysts is only temporary. If the fabrics are not given an alkaline afterwash, the methylamine held on the fabric in the form of acid salts may be liberated in use.

Lightfastness of dyes. When dyed cottons are creaseproofed, the lightfastness of dyes may be affected, sometimes adversely, though no definite evidence of chemical reaction between creaseproofing compounds and dyes has been found [23, 24, 48, 49, 72, 89, 101, 218, 266, 269, 274, 434, 658]. Dimethylol urea has a small and dimethylol ethylene urea a severe effect. Metal-salt catalysts exert a protective action while amine and ammonium salts affect lightfastness unfavorably.

One possible explanation of the reduction in lightfastness is that the creaseproofing materials absorb a fraction of the total spectrum, and what is left does more damage than the original light. That a fraction of the total incident light can do more damage that the whole, the principle of radiation antagonism, has been demonstrated. Another possible explanation is that the dye generates hydrogen peroxide photochemically, and this compound can liberate free radicals from the cross-linking material. Free radicals can reduce quinoid groups of dyes and thus cause color loss.

Improvement in Cotton's Wrinkle and Deformation Recovery: Processes

Treatments to impart recovery from deformations can be applied to all cotton textile products. Originally, creaseproofing processes were applied primarily to woven cotton fabrics; the treatment of knit cotton goods has become popular in the late 1950's. Treatments imparting recovery from deformation are also utilized to produce pleated goods and fabrics having unusual surface effects.

While deformation recovery and other properties of creaseproofed cotton depend largely on the materials used in the treatment, processing conditions also affect the final properties of the finished product. The important effect of fiber distention during the reaction has been mentioned previously. Other process variables, such as uniformity and extent of impregnation and temperature and duration of the drying and the curing steps, must all be properly chosen to produce the optimum product [25, 29, 38, 147, 194, 225, 226, 227, 240, 293, 361, 368, 416, 453, 477, 580, 604, 659, 668, 686, 724, 750, 764, 769, 771].

Conventional Method

Conventionally, fabrics are first impregnated in a pad box; excess liquid is squeezed out; the fabrics are then framed, dried, and cured. In many plants the cured fabrics are afterwashed, sometimes with bleaching.

Pretreatments. Greige goods are generally subjected to the usual preparing and finishing operations, including coloring, prior to creaseproofing. However, simultaneous dyeing and creaseproofing is possible, and a commercial process of this type has been described in 1960 [163, 371, 424]. The process employs dyes capable of reaction with and attachment to cellulose or the treating agent.

Of the preparing operations, mercerization is of particular importance, because it renders fabrics more absorbent. However, if the mercerized material is overdried, many hydroxyl groups become strongly hydrogen bonded and the fibers may be actually less accessible than untreated cotton [726]. Mercerization improves fabric elastic recovery, but this advantage does not survive conventional creaseproofing [408, 546].

Many special pretreatments have been suggested. Treatment with ethylamines reduces fiber crystallinity and nearly doubles elongation-at-break [309]. Since decreased extensibility is an undesirable result of cross-linking, it has been suggested that an amine pretreatment may compensate for it. Experimental work on this idea did not, however, produce improved materials. Other proposed treatments include chemical modification of cotton, such as carboymethylation [167, 168, 379, 586], hydroxyethylation, cyanoethylation [143], carbamylation, phosphation, and partial esterification [501]. Carboxymethylation is claimed to give particularly good results. The acid groups present in the fabric catalyze cross-linking, thus eliminating the need for catalysts, and high swellability of pretreated fabric permits good penetration of treating agents. Pretreatment with acid solutions has been patented [52], and carboxyl groups can also be introduced into the cotton fiber by half-esterification with dicarboxylic acids or their anhydrides, such as maleic anhydride [243, 356]. However, none of the special pretreatments has achieved commercial acceptance.

Impregnation. Fabrics being treated must be clean. Residual alkali can neutralize acid catalysts, and this may result in undercured or nonuniformly cured products [361]. Other materials which may have been applied to the fabric, such as starches [120] and dye-fixing compounds, may also interfere with the reactions and must therefore be removed prior to the treatment.

The moisture content of fabrics going into the bath must also be considered. Swollen fibers absorb the solution better, but the water present in the fibers has a diluting effect, lowering the effective concentration of the treating agent [406, 791].

In the pad box, excess solution is squeezed out under a pressure calculated to give the desired wet pickup. Three bowl padders are preferred because a more complete and uniform fabric penetration can be obtained with two consecutive dips and nips. The use of wetting agents and high nip pressures has been recommended to insure penetration of the treating solution into fibers [591]. However, pressure cannot increase fiber absorption capacity. With the usual 80% wet pickup, only 30% can possibly be held by fibers; the other 50% must be held in the capillaries between fibers and yarns. It has been suggested that moisture in these capillaries evaporates rapidly on heating so that the formulation held outside fibers becomes more concentrated than that within them; because of this concentration gradient, molecules of the reagent diffuse into the fibers during drying and curing [561]. Treating formulations can be applied to fabrics simply by spraying [43].

Drying and curing. Impregnated fabrics are usually dried at moderate temperatures before curing. This is done to reduce the loss of volatile reagents [31] and to minimize surface resin deposition ascribed to "migration" of reagent molecules to fiber surfaces [62, 328].

Use of clip tenters and rope-handling of goods are among practices dictated by the economics of the process, which requires high-speed production. Application of tension has been suggested as a means of improving tensile properties [277, 316, 317, 401, 526, 527, 723]. However, methods which do not strain fabrics, though more time-consuming, have much to recommend them [155, 413]. In addition to improving wrinkle resistance, treatment in relaxed condition results in higher dimensional stability upon subsequent laundering [685]. Release of stresses on washing may result in "pebbled" appearance, and dimensional stability is important for woven fabrics and vital in knit goods.

The most popular curing medium is hot air [33], but other media have been suggested. Curing with superheated steam containing a relatively high proportion of moisture has been claimed to give fabrics having a higher abrasion resistance than fabrics treated in dry heat [299, 445, 446, 671, 768]. Experiments with ultrasonic [95], inert liquid [538], fluid bed [51, 357, 444, 592], infrared [734], multifrequency [22], and high-frequency [37, 44, 162, 496] curing have also been made.

The degree of cure attained is of utmost importance because wrinkle recovery level, chlorine damage, and finish durability depend on it [10, 303, 604, 607, 659]. Too "mild" a cure may result in incomplete reaction and formation of side chains and polymeric materials. This leads to products having poor, not durable wrinkle resistance and high chlorine retention. On the other hand, overheating may degrade both cotton and the agents and lead to excessive tensile loss and formation of odors in the finished fabric.

Aftertreatments. Cured fabrics are normally afterwashed for quality finishes. Evolution of formaldehyde from finished fabrics is diminished by this step, as is the possibility of fish-odor formation [294, 576]. Afterwash should be alkaline to break down amine salts and permit the free amines to come off the fabric during hot rinsing. Alkaline afterwash will also neutralize any catalyst left in the fabric. This will help to avoid post-curing, which can result in formation of permanent creases in folded and bolted fabrics [492]. It will also diminish finish hydrolysis, which leads to a lower wrinkle-resistance level and higher chlorine damage in fabrics treated with N-methylol compounds [46, 582].

Treated fabrics may also be subjected to aftermercerization, particularly if the treatment has affected tensile and tear strength unduly. Aftermercerization improves these properties and increases moisture regain to an extent which more than compensates for the decrease caused by cross-linking [152, 153, 154, 457, 583]. It is not an unmixed blessing, however, since it also removes some of the finish.

Another remedy for the excessive strength loss is stripping the finish and refinishing. This method is most suitable for reagents which react with cellulose through the N-methylol group, since they can be stripped under conditions which do not damage cotton [629].

The Wet-Cure Process

Processes which produce wet-only wrinkle resistance differ from the conventional process essentially in that the reaction takes place in swollen fibers. In the dichloropropanol treatment, the fabric is subjected initially to the usual finishing operations, including mercerization. It is then impregnated, without drying, with caustic and the treating agent [104]. Several processes of this type have been described [113, 182, 229, 247, 340, 628, 753, 754, 755].

According to a description of a wet-cure process using formaldehyde, the fabric is treated in aqueous solution of this reagent and sulfuric acid [97, 482]. It is steeped in the solution, the duration of steeping depending on acid and formaldehyde concentration and on temperature. The fabric is then washed and dried. Other processes, some of which offer the possibility of controlling fiber swelling through control of the water content of the reaction medium, have also been disclosed [126, 572, 573, 617]. A mild pretreatment for conventional creaseproofing uses an aqueous solution of formaldehyde and hydrochloric or formic acid [292].

Processing of Knit Goods

Treatment of knit cotton goods with creaseproofing formulations became popular in the late 1950's. Because of the inherent high degree of fiber and yarn mobility, knit goods have good wrinkle resistance. The treatments, however, impart dimensional and shape stability to the fabrics, in addition to enhancing their wash-and-wear characteristics. This is an important achievement, since knitted fabrics cannot be adequately stabilized by mechanical treatments.

The basic processes for treating knit goods are the same as those for woven fabrics. However, the effort made not to distort the goods is even greater, and the processes differ in a number of important details [40, 41, 272, 351, 575].

Pleating

Just as a fabric cured in the flat state maintains its smooth appearance, so a fabric cured in the pleated form maintains the pleats in wear and laundering. This is the basis for continuous pleating of cotton fabrics for skirts and similar apparel use. One such process consists of passing the impregnated and partially-dried fabric through a pleating machine whose rollers are maintained at a temperature high

enough to cure the treating agent [160, 796]. In another, the impregnated fabric is pleated and then cured with hot gases while in a tensionless state [64]. Methods for inserting warp-wise [106, 336] and "sun-ray" [159] pleats have also been disclosed.

Surface Effects

The ability to maintain cured-in shapes conferred on cotton by creaseproofing has been utilized to produce special surface effects by a calender-and-cure process performed on impregnated partially-dried fabrics [30, 68, 98, 211, 377, 414, 419, 437, 497, 518].

The sheen of polished cottons is not due to a deposit of "polished resin" on the surface of the fabric [509]. Even without resin, cotton can be given luster by calendering, which flattens the yarns and gives the fabric a smooth surface. This luster, however, does not last through washing, because fibers swell in water and the fabric surface after drying is no longer smooth. The treating agents confer on the fibers an ability to maintain the shape in which they were cured, and thus make the effects of friction or Schreiner calendering durable. The same principle holds true in embossing, where the function of the treating agents is to prevent fiber deformation which would destroy the three-dimensional surface effects.

Calendering and similar mechanical treatments affect fabric geometry. The basic considerations discussed in the section on fabric construction also apply to such treatments: if they decrease the freedom of fiber and yarns to move, they diminish fabric wrinkle resistance. Fabrics compressed normal to their plane, i.e., flattened out, are less wrinkle resistant than the same fabrics prior to the treatment [413]. This effect can be prevented, however, if the fabrics are simultaneously compressed both parallel and normal to their plane, as in a process in which the fabric is first impregnated, then dried to the desired moisture content, and finally compressively shrunk and heat cured at the same time [403, 404, 556]. Such processes, however, are incidental to creaseproofing, and will not be described here more fully [65, 130, 222, 612, 689, 756].

Yarn and Fabric Construction

Fabrics made from the same fiber but of different constructions may differ by over 50% in crease recovery [387]. The selection of appropriate yarn and fabric construction is, consequently, extremely important for the deformation recovery of the final product [301, 302]. Of course, the usual considerations of utility and beauty must not be disregarded, nor is it possible to ignore customs of long standing. However, all textile constructions are the result of compromises among the many requirements made of the end product. Recovery from deformation is today an important consumer requirement, and special attention should be paid to factors which favor it.

For optimum deformation recovery, textiles must be so constructed that the total strain on fibers (strain imposed by preparatory processes combined with strain imposed by external stresses) does not exceed their recovery limit. Accordingly, changes in construction which lead to low fiber strain in the "ready for use" state, and to a decrease in transmission of applied stresses, generally lead to better deformation recovery. However, while this holds generally true for conventional cotton fabric constructions, it is not true for all textiles. If an external stress applied to the textile is completely dissipated by displacing fibers and moving them past each other, recovery will be poor [164]. When the external stress is removed, the textile will remain deformed, because the fibers will not move back to their original positions. In such fabrics, deformation recovery is improved by changes in construction which permit the fibers to assume a larger portion of applied stresses.

Fiber Properties

The ability of fibers to recover from deformation is the basis of deformation recovery in textiles, and more resilient cottons give somewhat more wrinkle resistant fabrics. However, the differences among various cottons level out in the course of manufacturing and finishing operations, and the differences among fabrics are not highly significant [562, 564, 565].

It must be emphasized that for wrinkle recovery in fabrics it is the ability of fibers to return to the configuration in which they were held in the flat fabric that matters. Fabrics made from synthetic fibers of high intrinsic resilience do not have a high wrinkle recovery as they come off the looms. The residual fiber strain in the flat fabric may be so high that when an additional strain is imposed the total exceeds the limit of recovery. It may also be that fabric deformation relieves strains on some fibers, as when the applied torsion untwists a yarn. Both

processes may operate concurrently, on different fibers.

The high wrinkle resistance of fabrics made from thermoplastic synthetic fibers is attained by subjecting them, in the piece, to "heat setting," which relieves strains introduced by spinning and weaving. The fibers' new "least-strain" configuration is that which they have in the flat fabric, and this is the configuration they tend to maintain. Similarly, worsted fabrics are subjected to crabbing, a process in which heat and moisture relieves the "hydroplastic" wool fibers of strains introduced by the preparatory processes.

In treated cotton, cross-linkages stabilize fibers in the configurations in which they happen to be during the treatment. If the treatment is applied to a flat, smooth fabric, this is the shape to which it will tend to return. Fabrics made from previously cross-linked fibers are loftier than fabrics treated in the piece, because the more resilient cross-linked fibers cannot be spun and woven as tightly as native fibers, but they are not highly wrinkle resistant [362].

It has been suggested that coarse, stiff fibers, which resist bending better than fine ones, may yield fabrics with improved wrinkle resistance. This is still a controversial point. Apparel fabrics cannot be so stiff as to resist bending in use. It is often said, therefore, that it is not the ability to resist bending forces but the ability to return to prestressed configurations that is important [674]. However, some deforming forces which act on fabrics in use may be so low that resistance to bending may be of value.

Similar considerations apply to fiber shape [150]. Fibers of circular cross section resist bending better than ribbon-shaped ones. However, strains imposed by bending about an object of the same diameter will be higher in coarse fiber than in a fine one, and the circular fiber will, in effect, behave as if it were coarser.

The effect of staple length on fabric wrinkle resistance is not important provided the fibers are long enough to permit optimum twist.

Yarn Construction

Of the factors involved in yarn construction, perhaps the most controversial one is the degree of twist [57, 149, 241, 270, 313, 333, 542, 543, 544, 636, 666, 702, 770]. On the one hand, low-twist yarns can be more easily penetrated by treating solution; fibers in low-twist yarns are under a smaller strain than fibers in highly twisted yarns [540, 541]; lateral forces between fibers in low-twist yarns are smaller than those in highly twisted yarns, and this affords mobility and permits buckling and flattening. A yarn capable of flattening becomes wider and thinner at the apex of a bend, the radius of curvature increases, and strain on fibers, which depends on radius of curvature, diminishes.

On the other hand, yarn flattening increases fabric cover factor and, because there is less space between the wider yarns, mobility is reduced. Low twist also reduces frictional forces which bind fibers in yarn, and this may lead to excessive fiber slippage. A low-twist yarn is less extensible, within a certain range at least, than a high-twist yarn, and for low-twist yarns the increase in fiber strain due to bending is higher than that for high-twist yarns. The highly twisted yarns apparently dissipate applied stresses more efficiently.

Twist affects the directional wrinkling behavior of fabrics. Bent yarns are subjected to torsional forces. It has been suggested that if the twisting forces act in the direction of the twist already on the yarn, recovery will be enhanced; however, if they tend to untwist the yarn, recovery will be decreased because the untwisting will stabilize the wrinkled configuration [672]. This may lead to anisotropic creasing behavior.

The use of yarns twisted in "S" direction for warp and in "Z" direction for filling has been suggested as a method for improving fabric recovery. In such fabrics, yarns slide over each other more easily because "nesting" at crossover points is diminished. The improvement attainable is highest if warp and filling yarns are of approximately the same size.

Yarn size is of considerable importance since the average strain per fiber in bent as well as in unbent yarns depends in part on the number of fibers under stress in a yarn. Also, by substituting heavier for thinner yarns, one may produce fabrics with equal weight but more open texture.

Fabric Construction

Wrinkle recovery is strongly influenced by fabric construction [47]. The most important parameters seem to be thread count and float length, the first being the more important of the two. Among the advantages of low-count, high-float fabrics are longer intervals between yarn crossovers; these lead to lower interyarn friction and more yarn flexibility,

so that buckling and float bowing are easier. Crimp interchange and bending stress distribution are also favored by longer distances between yarn crossovers.

Improvement obtainable by decreasing yarn density approaches a limiting value beyond which further improvement cannot be obtained. Strain can be spread only over a certain yarn length; there is only a certain degree of mobility necessary to permit buckling, and further decrease in fabric density has no effect. This point of diminishing returns is reached sooner with basket or twill-weave fabrics than with plain-weave fabrics. In the more complex weaves, yarns have a higher degree of mobility to start with, and they need less additional freedom to reach the optimum condition than do plain-weave fabrics. Similarly, improvement in wrinkle recovery attainable by increasing float length is higher with tightly-woven than with more open fabrics.

In plain-weave fabrics, which have the maximum number of interlacings of both warp and filling yarns, fiber strains in the fabric are higher than in a 2×2 basket weave, where two yarns weave together and their paths are therefore not quite so tortuous. The longer floats of the 2×2 basket weave give, in effect, an increase in the distance between yarn crossovers similar to that obtained by a decrease in fabric density. In fabrics whose warp and filling yarns do not appear for equal lengths on both face and underside, as in a 3×1 twill, strain imposed by bending varies depending on the direction of fold, and such fabrics are most suitable for end uses in which creasing is likely to be directional. The longer float should be on the outside and perpendicular to wrinkles formed in use, to take advantage of the greater ease of buckling of the longer yarn span. In fabrics for end uses in which wrinkling is likely to be random, even-sided weaves are probably more satisfactory.

The interrelationship of various construction factors is complex. The generalization that increased mobility of fibers and yarns leads to improved wrinkle recovery of fabrics is quantitatively expressed in the so-called "tightness number," defined as the number of yarns per inch of fabric divided by the number of yarns per weave repeat in basic weaves [387]. The number of yarn crossings per square inch of fabric has also been suggested as a useful index of "openness" [663]. Development of a more accurate index must await a clearer understanding of the contribution of each construction parameter to the total fabric performance.

Tear and tensile strength. Fabric construction factors which favor wrinkle recovery also favor tear strength, fiber and yarn mobility being necessary for both [47, 349, 677, 709]. Thus complex weave and low yarn density are desirable for good tear strength; for example, a change from a plain weave to a 2×2 basket, other factors remaining unchanged, can triple the tear strength of a 3-oz. fabric [670]. High tensile strength, on the other hand, can be obtained by using a weave with the highest possible number of interlacings per weave repeat and high yarn density since it depends largely on cohesive forces between fibers [708]. A compromise between these mutually contradictory requirements must be made each time a fabric is designed, and all too often the solution favors tensile strength at the cost of tear strength and wrinkle resistance. Because it is easy to measure, tensile strength has been used for years as a criterion of fabric quality. However, it is not necessarily a good indicator of serviceability.

Testing Methods and Equipment

The deformation recovery of a textile article in use is a complex function of mechanical properties of fibers of which it is made; construction factors; direction, magnitude, and duration of stresses to which it is subjected; and environmental conditions. In research and development work it is often necessary to measure the contribution of each of the individual factors involved, but the ultimate criterion is performance in use [84].

Mechanical Properties

Stress–strain curves. Elastic recovery of fibers, yarns, or fabrics can be determined by subjecting them to extension–recovery cycles. Rates of extension, loads used, and other parameters of the test can be varied, and the stress–strain or load–elongation curves obtained provide a wealth of information about the tested specimen's response to stress [42, 171, 388, 657]. However, the wrinkling behavior of textiles is not fully defined by stress–strain curves.

Resilience. Resilience, defined as the ratio of energy expended by the recovering textile to energy required to deform it, has been suggested as a good index of fabric ability to recover from bending

stresses [623]. An instrument designed for measuring this property consists, essentially, of a clamp holding one end of a specimen and a sensitive balance supporting the other end [615]. The clamp can be deflected; the force on the balance necessary to compensate for this deflection is a measure of the resistance of the fabric to bending. By increasing the deflection to a certain predetermined point and then decreasing the load, one can obtain curves showing the load-vs.-deflection characteristics of the material. The area under the curve obtained for the loading half of the cycle represents the amount of work required to deform the fabric; the area under the "return" curve represents work done by the fabric in recovering from the deformation; the area between the two curves represents mechanical hysteresis, and is related to permanent set.

A similar procedure has been devised for studying the behavior of fabrics in bending when the bending radius varies from about 1 cm. to fabric thickness, as it is when the fabric is creased [674]. A fabric strip 1.5 cm. wide and 7.5 cm. long is formed into a ring by cementing the two ends together on a microscope glass slide. The slide is placed on the crosshead of an Instron tensile tester. A weight to which another slide is attached is placed directly over the loop. The weight is fastened to a strain gauge. In testing, the crosshead is moved at a predetermined rate, and the fabric ring gradually assumes the load of the weight. By plotting the logarithm of the distance between the slides vs. the reciprocal of the load, curves describing the load–deformation characteristics of the sample are obtained. When the crosshead is reversed the curve describes the recovery. The interpretation of the curves is the same as described above.

The Flexometer and the Compressometer [623] depend on the same principle, as does a more recent Swedish instrument [191, 192]. In the first instrument, the torque exerted by a pair of fabric specimens as they resist being folded between two plates is the measured quantity. The total energy expended in folding the specimens to a minimum angle, as well as the energy recovered when the specimens are allowed to unfold, is determined. In the Compressometer, a fabric specimen is mounted, accordion-wise, on a special support, and again the energy required to compress it and that recovered in unloading are determined. The ratio of the energy recovered to the energy expended is the "compressometer flexural resilience." In the Swedish instrument, the fabric specimen is held in two clamps, one fixed and the other floating on mercury. A magnet with a moving coil is placed above the clamps. The fabric specimen is bent as the coil rotates about a vertical axis. Flexural rigidity of the fabric is defined as the product of the bending moment and radius of curvature. Another instrument developed by the Swedish workers determines the bending recovery of fabrics by measuring the radius of curvature of specimens first bent into a semicircular arc and then permitted to recover.

A somewhat similar method for determining the "resilient stiffness" of fabrics, i.e., their ability to spring back after the bending force is removed, has also been proposed [514]. The test is said to give a quantitative expression of the "hand" of a fabric when it is gently flexed between the fingers. A fabric sample is formed into a loop, and a weight is applied, deforming the loop to a predetermined extent. The force required is a measure of fabric stiffness. Then additional weight is applied to deform the fabric further. After a few minutes the weight is gradually diminished until the fabric loop assumes the first *deformed* position. The difference between the final and the original weights corresponds to the stress decay (creep) which occurred while the fabric loop was under stress.

Wrinkle Recovery

While resilience may be the basic factor in wrinkle recovery, determination of recovery from deliberately introduced folds gives a more direct measure of this property. Many tests have been devised to this end [151, 196, 215, 466, 553, 555, 626, 704]. Perhaps the simplest consists of making a ball from a small piece of fabric, squeezing it hard in one's hand, and examining the appearance of the sample upon release. In the simplest of the quantitative tests, a fabric strip, after creasing, is placed flat on its face on a board. The upper end is permitted to rise, and the recovery is measured in degrees by setting a protractor next to the strip. In another test a strip of fabric is pleated and placed under a weight for a certain period of time. The load is removed and the strip suspended by one end. Recovery is measured by the ratio of the length of the pleated strip to the original length of the specimen.

In the Tootal, Broadhurst, Lee (TBL) test, a fabric strip is folded in half across its narrow dimension and placed under a weight. It is then allowed to recover while hanging at the crease on a taut, thin wire. The degree of recovery is given by the distance between the ends of the specimen. The only equipment necessary for this test is the weight, a thin wire, and a ruler, and it thus has the advantage of simplicity. However, because the distance between the ends of the specimen is not a linear function of the crease angle, the test is inherently insensitive at good recovery levels. Also inherent in the test, in which the specimen is left free to hang on the wire, are difficulties with measuring the true distance between the ends. The hanging sample may twist, and the free-hanging ends are affected by gravity and tend to bend. Stiffer and lighter fabrics are less affected by gravity than limp and heavy ones, and this effect is more pronounced at wider angles than at small ones. Another variable is introduced by the way the crease is made. Handling the specimen during transfer onto the wire is still another source of error.

The bending effect of gravity can be eliminated by floating the creased strip on its edge on the surface of a liquid in which it will not sink. Mercury is nearly ideal for this purpose, but even mercury is affected by the atmosphere, and the condition of the surface of the liquid affects the results. Glass and other highly polished materials, which present little frictional resistance to the motion of the strip, have also been used.

The Shirley Institute developed a modification of the TBL method [27]. Still further modified, it is known in this country as the Monsanto test [16, 478]. The specimen is creased in a special holder, which is then inserted into the instrument together with the specimen. This eliminates errors due to manual handling of the stressed strip. The specimen is suspended in the instrument in such a manner that the section on one side of the crease is held firmly in the holder, while the other section hangs free. To eliminate the effect of gravity, the instrument is adjusted continuously by the operator or by an electronically-controlled apparatus [651] as the fabric strip opens, so that the free end is always aligned with a vertical guide line on the panel.

In the Roller Pressure Crease Tester [15, 172], a further refinement on the same principle, both the creasing step and the angle-reading step are more exact, and all need for manual handling of the specimen is eliminated. The specimen is creased by passing it, looped double, between two rollers. One of the rollers is driven at the desired speed and the other roller is idle. This roller can be made to press against the driven roller by a weight-and-lever arrangement. The amount of pressure applied to the fabric can be easily and exactly regulated because it is applied only at the point of contact. After passing through the rollers, the strip drops on a knife-edge fence located directly beneath. The recovery angle is measured precisely at the apex by means of a special optical system in which light directed parallel to the plane of the surface of the specimen throws its silhouette on a screen. Because the angle is measured at the apex, the drooping of the free ends of the strip does not affect the results.

Long-term recovery. It is occasionally desirable to determine the long-term recovery of fabrics. In practical terms this determination relates to the ability of a garment to rid itself of wrinkles while hanging in the closet. The British "Tentative Textile Standard No. 44" [100], which is based on the Shirley-developed technique, lists two methods. Method A provides for a 3-min. period under load, followed by a 3-min. period of recovery. In method B the specimen, having been subjected to the Method A test, is hung on a taut, thin horizontal wire for 1 hr., after which it is again placed in the instrument and the recovery angle is read immediately. This gives two determinations for one sample of fabric. The test may, of course, be repeated many more times; the results, plotted as recovery vs. time, give a more complete picture. Attempts have been made to develop a formula which would permit extrapolating such a curve on the basis of only a few determinations [661, 762, 763, 765, 778].

Wet wrinkle recovery. The Monsanto test is usually performed on conditioned fabrics at standard conditions for textile testing, 65% RH and 70° F. The effects of higher temperature and humidity on wrinkle recovery, important for fabrics meant for summer use, are sometimes determined by conditioning and testing the fabric at 90% RH and 95° F. Another modification of the testing procedure, intended to provide an indication of the fabric's wet wrinkle recovery, has also been proposed. The fabric specimen is wetted out, blotted to remove excess water, and then tested in the usual

manner [405, 454]. In a more severe variation of this method, the sample is soaked in water and then placed overnight under the creasing load between blotters [678]. The next day its recovery is measured on the Monsanto apparatus. The results have been reported as "dried-in" crease recovery.

The wetted-out fabric strips used in testing wet recovery are heavy, and the effect of gravity on the free hanging leg of the specimen is pronounced. The Monsanto-Quehl method combines the convenience and accuracy of the former with the vertical-crease principle of the latter [45, 737]. The Monsanto specimen holder is slightly modified to accommodate 1.5 × 3 cm. fabric strips, and the apparatus is maintained with the panel in horizontal position during the test. After the 3-min. recovery period is over, the wheel is turned so that the free leg of the specimen coincides with the zero guide line and the angle of recovery is read off the scale.

Another instrument in which the specimen is recovering under water and is so positioned that the crease is in the vertical plane has also been described [291]. The specimen is placed in water in a special holder. It is then folded and kept under a weight for the desired length of time, with the crease in the horizontal plane. The weight is then removed and the holder with the specimen is turned on its side. The degree of recovery is read against a scale marked on a brass plate attached to the specimen holder.

Of the many wrinkle recovery tests the one most popular in this country is the Monsanto test. It has been adopted by the AATCC (66-1959), ASTM (D1295-53T), ASA (L-22), the Federal government (Fed. Spec. CCC-T-191), and is used almost universally in the industry.

Appearance Tests

In recent years much work has been done to develop tests which give results in terms of consumer acceptability [246, 493, 588, 589]. The emphasis changed from objective determination of a mechanical property of the fabric to a subjective, visual evaluation of its appearance. The finisher is expected to produce a fabric which, made into garments, will meet the performance levels expected by the consumer.

The mechanical wrinkle recovery tests are useful in comparing the effects of various creaseproofing formulations on a given fabric, or on fabrics of similar constructions. They are useful in determining the relative effects of laundering and other chemical and mechanical treatments on the same wrinkle-resistant fabric, but they have not been found consistently dependable for predicting the subjective performance levels of different fabrics. The very refinements which make the mechanical tests accurate and reproducible also take them further away from what they are meant to test. For example, in spite of the wide acceptance of the more precise and reproducible Monsanto test, claims have been made that the TBL system gives results which correspond better with actual garment performance [361, 668]. In the TBL system the creased strip must open up against the force of gravity, which resembles what happens when a wrinkled garment is hung up more closely than in the Monsanto test. Similarly, the roller pressure method may indeed compensate for the differences in compressibility of various fabrics and distribute the load more uniformly, but in actual use there is no compensation for these differences.

Appearance factors. The lack of correspondence between mechanical tests and visual evaluations is due primarily to the fact that wrinkle recovery is not the only factor involved in appearance. Dimensional stability of the fabric, for example, affects its appearance after laundering [779]. In a poorly stabilized fabric, wetting releases strains introduced by the preparatory processes. This may result in formation of small ripples on fabric surface, which then will no longer appear as smooth as before, even though the fabric was not folded or bent in any way. It is obvious that no mechanical wrinkle recovery test can predict a change of this type.

Subjective evaluation of smoothness also involves psychological factors. The character of the surface of the fabric, its luster, its color and depth of shade, and the print pattern all affect the visual impression it gives [595]. The importance of the effect of print patterns has been strikingly illustrated by an experiment in which an attempt was made to correlate wrinkle resistance of fabrics as measured by a mechanical method and as evaluated subjectively in terms of "need for ironing" [782]. When data from the mechanical and the subjective evaluations were compared, no correlation could be found (Figure 19a). However, when the comparison was limited to fabrics which had symmetrical prints, with small patterns and large unbroken background areas,

the relationship became highly significant (Figure 19b). Fabrics with "busy" prints, with nonsymmetrical patterns, or with small unbroken background areas and contrasting colors, were found difficult to judge, and were generally classified much higher by the panel than by the mechanical recovery tests. Wrinkles are less easily perceived on a fabric printed with irregular or abstract patterns in a light shade than on one dyed a plain deep color. It may also be that certain fabrics are expected to appear smoother than others. For many men, for example, the standard of smoothness for a white broadcloth is higher than that for a denim.

Subjective appearance tests. The human eye can tell the difference between two adjacent areas if one is 1% more luminous than the other, and it is even more sensitive to differences in color [341]. Very few optical instruments equal the eye in this respect. Accordingly, several appearance evaluation methods consist simply of viewing the tested specimen under some specified condition and assigning a rating to it.

But while the human eye is very sensitive, quantitative subjective estimate of a change in an object is in most cases not a direct but a power function of the change [688]. The eye is, therefore, most dependable if it can compare objects before it. For this reason some organizations conduct the tests so that the viewers rate two or more specimens shown to them simultaneously under the same lighting conditions. Other popular evaluation methods depend on comparing the appearance of the specimen, or photographs of the specimen, with a series of photographs of various standards or with three-dimensional replicas of standards.

According to one test method of this type, developed by the Wash-and-Wear Committee of the American Association of Textile Chemists and Colorists, fabric specimens are placed flat on a table and three trained observers rate each specimen independently [588]. The lighting conditions, the position of the observer with regard to the specimen, and the light source are all controlled. The specimen is illuminated by a light striking it at a low angle. This minimizes the effect of color and pattern and permits the viewer to detect even small distortions. The observers grade the samples using a scale of 1 to 5, with each numerical value corresponding to the number of a photograph or a three-dimensional replica of a standard specimen (Figure 20) [36]. Many other "standards" for wash-wear or wrinkle-resistant cottons employ similar procedures [188, 417, 427, 627, 669, 695, 781].

The panel test method can also be used for evaluation of garments. Such tests evaluate the appearance

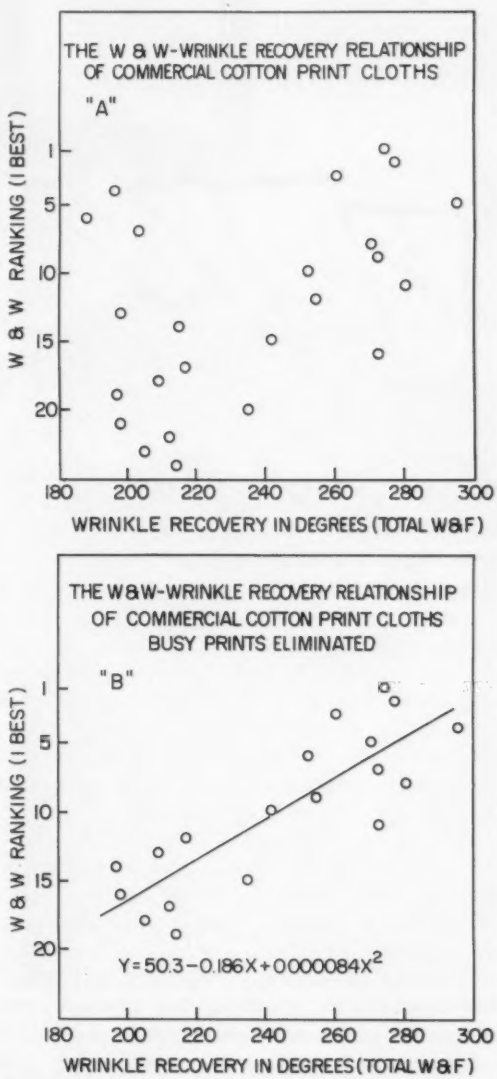

Fig. 19. A: When data from mechanical evaluation of wrinkle resistance of commercial cotton prints was compared with data obtained from subjective appearance tests, no correlation could be found. B: However, the relationship became highly significant when the comparison was limited to fabrics with symmetrical prints, small patterns, and large unbroken background areas.

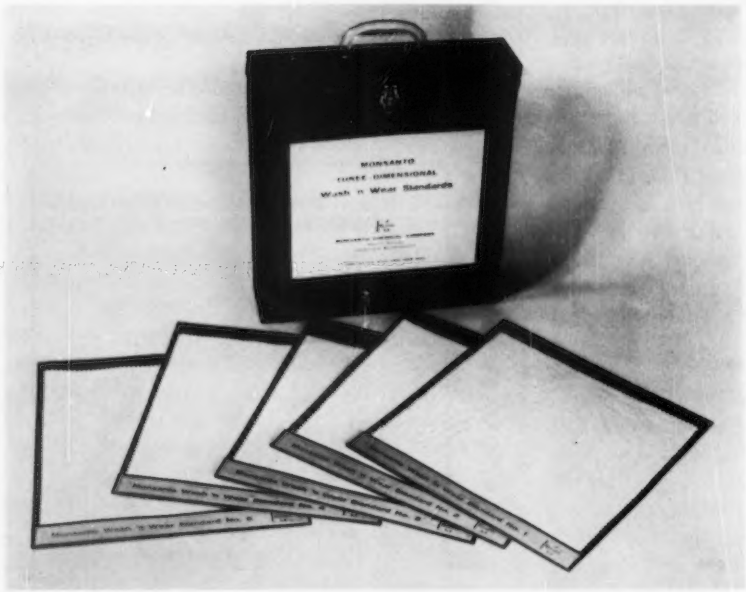

Fig. 20. Three-dimensional replicas of wash-and-wear standards.

of the whole article, including such factors as seam pucker, to which only a reference will be made here [67, 187, 305, 307, 534, 589, 645, 725]. In one test, three observers view the specimen illuminated by a light striking it at a 45° angle from a distance of 6 ft. [773]. A more sophisticated evaluation method depends on placing the garment to be tested in a dark box and viewing it under gradually increasing amounts of light, or with the light intensity kept constant but with gradually increasing periods of observation [397]. This "threshold" approach depends on the assumption that the poorer the appearance the more easily it can be noted at low light levels or at short viewing periods.

Just as evaluation methods are made to resemble visual impressions received in use, so methods of introducing wrinkles are made to resemble actual use conditions [366, 776]. In a test designed to evaluate the appearance of wash-and-wear fabrics after repeated home laundering, four alternative procedures are given, each believed to correspond to a different method of washing and drying used commonly at home [17]. The first procedure corresponds to the wash-by-hand and drip-dry method. The other three are based on machine washing. In the first of these the specimens are taken out of the machine before the final spin cycle and are drip-dried; in the second, they are permitted to go through the complete washing cycle and are tumble dried; in the third, they are also permitted to go through the complete washing machine cycle, but are dried on the line. Volume and temperature of the wash-water and tumble dryer temperature are all prescribed in detail.

This test was designed for use in evaluation of all types of wash-wear products, and provisions are made in it for heat-sensitive materials. Thus, the test prescribes wash-water temperature of 105° F. for thermoplastic synthetic fiber fabrics because they acquire heat-set, difficult-to-remove wrinkles if washed at the higher temperatures used for cotton [495]. Similarly, the tumble dryer temperatures are limited to 160° F., and a cool-off period while

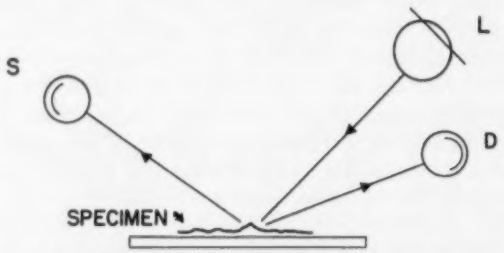

Fig. 21. Schematic representation of the Optical Wrinklemeter; L—light source; D—phototube measuring diffused light; S—phototube measuring reflected light.

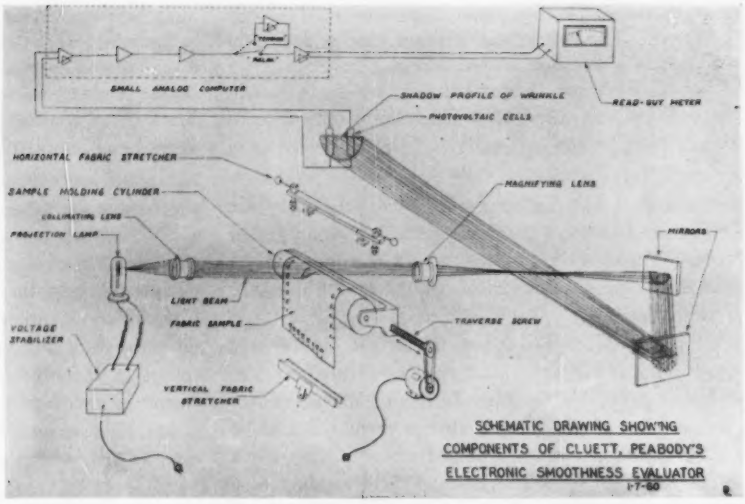

Fig. 22a. Schematic view of the Electronic Smoothness Evaluator.

tumbling is prescribed, again to prevent the formation of wrinkles in the synthetics. It should be pointed out that wash-wear cottons are not heat-sensitive and should be laundered at higher temperatures. Laundering at low wash-water temperatures is less efficient, and if used repeatedly may result in soil build-up [35, 656].

Objective appearance tests. Because of the human element involved, subjective appearance tests are inherently less reproducible than mechanical tests. Accordingly, efforts have been made to devise objective appearance evaluation methods [589].

Since the appearance of a fabric is determined by the direction, amount, and type of light reflected from it, it has been suggested that an apparatus measuring the reflectance of a fabric may provide means for objective quantitative evaluation of a creaseproofing finish. The Optical Wrinklemeter has been developed along these lines (Figure 21) [342, 417]. This instrument makes use of the fact that a flat fabric surface illuminated in near-grazing direction reflects more and diffuses less light than a wrinkled surface. An automobile spotlight illuminates a 4 × 6 in. area of the sample in near-grazing direction, and two phototubes, one on each side of the sample, are used to determine the amount of light reflected and that diffused. The ratio of the outputs of these phototubes is a measure of wrinkling.

The Electronic Smoothness Evaluator eliminates all dependence on the human eye (Figure 22) [34]. The fabric profile is scanned with a beam of light as the laundered sample moves continuously on a cylinder. Each 16-in. square sample is scanned along 8 warp and 8 filling positions. Deviations from absolute smoothness are translated into electrical current and computed in volts. The sample is then stretched on the cylinder, so that all wrinkles are

Fig. 22b. General view of the Electronic Smoothness Evaluator.

removed, and readings are taken on the smooth specimen. The difference between first and second readings is a measure of wrinkling.

The Low Angle Projection test, which is still in the development stage, also depends on optical techniques [83]. High-intensity light is projected at a 7° angle onto a surface. Because of the low incidence angle non-planar surface irregularities cast exaggerated shadows, which provide an amplified representation of the contours of the specimen. Upon analysis, these shadows yield a quantitative measure of wrinkling.

In the Wrinklometer the fabric sample is held steady on a movable platform by means of 5-g. weights suspended by threads from each corner of the sample [315]. The platform with the sample travels under a counterbalanced feeler probe which traces the contour of the sample. The probed contour is retraced on a chart, which provides a direct reproduction of every bump and valley on the sample. The mean wrinkle height, calculated by an electronic integrator from the area under the curve, is a measure of the degree of wrinkling. The British Cloth Profile Recorder, suggested for determining structural faults in fabrics, operates in a similar manner [116].

While the most widely used method of subjecting fabric specimens to wrinkling consists of laundering, mechanical methods of introducing random wrinkles in fabrics have also been developed. The Wrinklometer employs a glass test tube, into which the samples are stuffed randomly, and in which they are held for 3 hr. They are subjected to a constant pressure by means of a weight which is slipped into the tube on top of the sample. The somewhat similar Celanese Wrinkle Tester is designed to reproduce end-use conditions more closely [373]. It consists essentially of an interconnected system of tubes. Pumping air in and out causes rubber diaphragms in the tubes to set and collapse alternatingly. The diaphragms, on collapsing, wrinkle the specimens in a random manner. The pressure under which the samples are crushed, the rate of the alternating pressure–vacuum cycle, and the duration of the test, can all be controlled. In addition, the apparatus also includes a humidifier, which permits testing at various humidity levels.

Crease Retention

Crease retention is that fabric property which permits it to maintain an inserted crease in use. It must be pointed out that the term "crease retentive" is meaningless unless the test conditions are given: an untreated cotton fabric maintains a steam-pressed crease rather well even at high temperatures, but loses it on wetting, while a thermoplastic synthetic fabric maintains a heat-pressed crease even when wet, but loses it when heated. Crease retention should not be taken to mean the same as "creaseability," which can be defined as that fabric property which allows the insertion of durable creases. Creaseability is the opposite of wrinkle resistance. Cottons creaseproofed in the flat state have a high wrinkle resistance and poor creaseability, but the retention of cured-in creases and pleats in treated cotton is excellent.

Modified wrinkle resistance tests have been used for measuring both creaseability and crease retention [122, 244]. According to the most recent one, a crease is inserted in a fabric strip, which is then opened, placed between two glass plates, and subjected to a load of 2 kg. for 1 min. After a recovery of 1 min., the angle between the arms of the specimen is measured on the Shirley Creasing Tester. The ability of the fabric to retain a crease through laundering is determined by boiling the creased strip for 10 min.; placing it, with the crease vertical, on the bottom of a vessel containing water at room temperature; and measuring the angle between the arms of the specimen with a transparent protractor. This is followed by blotting the strip to remove excess water; subjecting it, opened and placed between two glass plates, to a load of 0.5 kg. for 1 min.; allowing it to dry while hanging at the crease on a thin horizontal wire; and again measuring the angle on the crease tester.

The Creasometer, an apparatus designed for evaluating crease sharpness and crease retention, permits the determination of the optical profile of a crease so that measurements can be made of its geometry [777]. Crease retention is expressed as the ratio of crease sharpness in the final state to initial crease sharpness.

Research Opportunities

Despite their many advantages, easy-care cottons on the market today fall short of the ideal, and the creaseproofing field offers many opportunities for rewarding research and development work. There is a need for improvement in the performance level of wash-wear cottons and for improvement in the dura-

bility of the finish to the drastic procedures of commercial launderers. There is also a need to develop means of avoiding the strength losses caused by present treatments and to develop a cheap and simple process for introducing durable creases into treated fabrics. Moreover, research is necessary to point the way towards exploiting improvements in cotton's recovery from deformation in products other than wrinkle resistant fabrics.

Many cotton finishers have by now acquired the skills necessary to achieve optimum results attainable with present materials and techniques. If major advances are to come, new reagents and processes must be developed. There is a need both for applied research and for a more fundamental approach to provide basic information from which fresh ideas can be drawn.

The Cotton Fiber

Structure. The extent of crystallinity and distribution of ordered and disordered regions in the fiber and the arrangement of molecules in microfibrils and between them, all require further elucidation. An investigation of the fiber at various stages of growth may throw light on the manner in which cellulose is formed and laid down in it. Electron microscopy, which was intrumental in providing much of what is already known about the fine structure of cotton, could be profitably utilized to this end.

Work on these problems will provide fundamental information necessary for improvement in cotton's deformation recovery. More precise information on the structure of the fiber, for example, may pin-point sites in which cross-linkages would give the greatest improvement .

Breeding. For many years cotton breeders have been working to develop strains having good strength, length, and fineness. Resilience has not been a major quality requirement in the past. Today, however, a large fraction of total cotton production is converted into wrinkle-resistant fabrics, and the ability of the fiber to recover from deformation has become an important consideration. An effort should be made to determine what are the fiber characteristics that make for good wrinkle-resistant fabrics and to develop cottons best suited for this use.

This work would involve an investigation of native as well as treated fibers, since the increase in fiber resilience attainable by creaseproofing appears related to the X-ray angle. In addition to resilience, the two properties which suffer most in creaseproofing, extensibility and strength, should be paid particular attention.

Deformation and Recovery in Cotton

The mechanisms by which native cotton fibers deform and recover from deformation require further clarification. Work on this subject would also be largely fundamental in nature, but it is essential to the development of cottons having improved deformation recovery. A more precise determination of the effect of structure on properties is of vital importance. A study should be made to establish physical properties of fibers produced under controlled and different conditions of growth and therefore differing from each other in thickness of layers, density of fibrils, interfibrilar distances, etc. Slippage between molecules, microfibrils, and growth layers and extension and rotation of spirals contribute to fiber extensibility, permanent set, and recovery. Information is needed on the contribution of each of these mechanisms to each of these properties. The data obtained may provide the basis for treatments tailored to affect only the chosen deformation and recovery processes, thus producing maximum improvement in recovery with minimum strength loss.

Many data are available on mechanical properties of cotton, but gaps still exist. In particular, there seems to be a need for information on the effects of changes in humidity. Better single-fiber testing techniques are required to overcome the difficulties connected with variability in cotton.

Improvement in Cotton's Deformation and Recovery: Mechanisms

Cross-linking and resin deposition. Many workers consider covalent cross-linkages essential in improving wrinkle resistance. On the basis of available experimental evidence, however, the possibility that resin deposition or side chain formation may also play a role in the process cannot be discounted. This question should be resolved. The effects of treatments with resin precondensates (both those capable and those incapable of reaction with cellulose), with nonpolymerizable cross-linking agents, and with compounds capable only of substitution on the cellulose chains should be determined unambiguously.

Work on the mechanism of improved wrinkle recovery in cotton is hampered by the lack of a method for introducing a measurable number of cross-linkages into the fibers. Perhaps the reaction of cellulose

with quaternary amine salts of bis-chloro-methyl ethers could be developed into such a method [500, 635]. The applications of compounds tagged with radioactive atoms, in view of the developments in tracer techniques, also holds promise.

Distribution of cross-linkages. More experimental evidence is needed to confirm the hypothesis of restrictive effect of cross-linkages in the disordered regions of the fiber and their disruptive effect in other areas. Information on the effect of cross-link location may contribute to the development of highly absorbent and yet quick-drying cottons having optimum wet and dry recovery.

Cross-linking of partially saponified acetylated cotton may be worthy of exploration as a method of determining the effect of location of cross-linkages. Saponification of acetylated cotton can be controlled without great difficulty, and products of almost any desired degree and distribution of residual acetyl content can be obtained [60]. It may even be possible to saponify the fiber to limited extent, cross-link it, and then continue the saponification. In this manner it may be possible to produce cotton fibers in which the distribution of cross-linkages would be predetermined and varied. Cross-linkages could be limited to the outer regions of the fiber, and the extent of cross-linking could vary from that limited to the most accessible regions to that permeating the entire structure. A study of the mechanical properties of such fibers would provide fundamental information on the effect of location and extent of cross-linking on deformation and wrinkle recovery. By varying the ratio and distribution of acetyl groups and cross-linkages one may produce cotton having a degree of thermoplasticity as well as improved deformation recovery.

It is also desirable to evaluate the properties of cotton fibers cross-linked only in the outer regions by treatment with acid colloids of resin precondensates. In addition to excellent rot and mildew resistance, fabrics treated in this manner may have unusual mechanical properties. A patent on cellulose-coated creaseproofed cottons has been issued [549], and a considerable amount of data is available on regenerated cellulosic fibers in which the outer regions and the core have different structures. This information should be utilized in the production and evaluation of skin-treated cotton.

Wet and dry wrinkle resistance. The mechanisms of wet wrinkle resistance require further study. The cross-link distribution hypothesis is supported by much experimental evidence, but it is not fully consistent with reports that heating in presence of acids converts high-swelling materials obtained by the wet-reaction with formaldehyde into the low-swelling cellulose obtained by the dry-cure method [428, p. 151]. If the high swelling capacity of wet-reacted fibers (and their high wet wrinkle recovery) results from cross-linking the less disordered fiber regions, this conversion is difficult to explain in view of the well-known stability exhibited by methylene ether cross-linkages. It has also been reported that the high-swelling materials have the property of combining with amines, amides, etc. [97]. This property, too, cannot be easily explained on the basis of the cross-link theory. Research is needed on the role played by cross-linkages and by hydrophilic substituents in dry and wet wrinkle recovery. Research is also needed to determine and differentiate between the functions of dry wrinkle resistance, wet wrinkle resistance, and recovery on wetting in the wrinkling behavior of a cotton fabric.

To attain optimum wet and dry wrinkle resistance, some finishers treat fabrics with both the wet-cure and the conventional process. A single two-step process may also give better results than the conventional method alone. The fabrics could be impregnated to a wet pick-up sufficient for the total effect, given a partial cure in the swollen state, and then dried and heat-cured. The degree of cure in each step could be varied to obtain optimum results. There is a need for a commercial process for crease-proofing cotton at the state of distention which produces best wet and dry wrinkle resistance.

Strength losses. Methods for eliminating, or at least minimizing, strength losses caused by crease-proofing should be developed. However, the importance of these losses in terms of wear life should be evaluated first, if for no other reason than to determine how much effort is justified. A systematic study of the abrasion resistance of fabrics differing in construction and treated with formulations composed of different reagents and lubricants is indicated. Both wet and dry abrasion should be tested, since the laundering process may have a significant effect on the wear life of apparel.

The possibility of decreasing tensile losses through the use of compounds forming long and flexible cross-linkages should be further investigated. It is necessary to determine whether it is possible to

modify cotton with long cross-linkages exhibiting flexibility, whether such cross-linkages improve cotton's deformation recovery as much as short-chain reagents, and whether the improvement in recovery given by flexible cross-linkages is attained at lower strength losses.

Esterification has been suggested as a pretreatment for cellulosic fabrics to be treated for wrinkle resistance, and lower tensile losses were claimed [242, 501]. The possibility of diminishing tensile losses in this manner should be investigated further. Since a part of the permanent set may be attributed to hydrogen bonds holding microfibrils in the stressed configuration, a decrease in the capacity for hydrogen bonding after creaseproofing may lead to a decrease in permanent set. Fewer cross-linkages might then give the required wrinkle recovery levels and tensile losses could be decreased.

External agents. The magnitude of the effect of softeners depends to a large extent on fabric construction, but the reasons why some fabrics respond better than others when treated with the same agent, and why the same fabric is benefited more by one agent than another, have not been established. If the various softeners act by different mechanisms, each would be more effective on fabrics on which the mechanism by which it acts has a better chance to operate. Experimental evidence along these lines would be useful to finishers.

Materials

Creaseproofing agents. An effort is needed to relate chemical properties of creaseproofing agents to their reactivity to cellulose and to finish durability. Substitution of electron-accepting groups on the nitrogen atom of N-methylol compounds and of electron-donating groups on the non-nitrogenous reagents should be attempted. A study should be made to determine whether N-methylol compounds can be made to resist hydrolysis without losing their ability to react with cellulose, and whether non-nitrogenous reagents can be made more cellulose-reactive without acquiring susceptibility to hydrolysis.

The relation between chemical properties of creaseproofing agents and their effect on lightfastness of certain dyes also awaits elucidation.

Materials likely to benefit the treated fabrics in more than one way should be among the compounds studied for use as creaseproofing agents. Phosphorous-containing compounds for possible use in finishes for both fire and wrinkle resistance should be screened. Efforts should also be exerted to develop mixed formulations which would permit a one-step application of multiple purpose finishes [138].

Treatment with compounds containing a reactive double bond may yield fabrics capable of further modification [794]. Allylated cotton can be cross-linked with ethyl acrylate [715]. The double bonds could also serve to anchor lubricants, soil-repelling chemicals, etc. Cellulose cross-linking dyes based on cyanuric chloride have been described [169, 200]. Further study of such compounds is indicated to develop materials which could be used commercially for simultaneous dyeing and creaseproofing [424].

The ideal creaseproofing agent, one which confers a high degree of deformation recovery at a low tensile loss, imparts no odors, exhibits no chlorine damage, resists both acid and alkaline hydrolysis, and is inexpensive and easy to apply, is still to be found.

Catalysts. Studies of mechanisms of cross-linking would necessarily involve a study of the function of catalysts. There is very little information available on the manner in which the catalysts act, and there is some evidence that their role in the reaction may well be more complex than that of simple acid producers. Degree of recovery attained, magnitude of strength loss suffered by fabrics, durability of finish to laundering, and odor formation all are affected by the types and amounts of catalysts used. Determination of the relation between chemical properties of catalysts and their effects on fabric properties is an important research objective.

The development of alkaline catalytic systems is another promising research objective. Hydrolytic damage to cellulose caused by acid catalysts is probably responsible for a part of strength losses exhibited by creaseproofed cottons. The development of an alkaline catalytic system would provide at least a partial answer to the strength-loss problem. The epoxide and epichlorohydrin compounds are capable of reaction with cellulose in an alkaline medium, and a patented process has disclosed the use of dichloropropanol and caustic. The reactions of these compounds with cellulose deserve further investigation. Cross-linking with onium compounds takes place in an alkaline medium, and this reaction also merits study.

Work on the catalysis of creaseproofing should include generally the cellulose etherification reaction, ethers being the most stable of cellulose substituents.

Processing

Pretreatments and impregnation. Of the many special pretreatments proposed for fabrics to be finished for wrinkle resistance, none achieved commercial acceptance. However, they deserve a more careful evaluation.

Both spray and vapor phase processes have been suggested as alternatives to padding, and they offer advantages not attainable otherwise [190]. Both could be applied to materials not well suited for treatments involving tension and pressure, including ready-made garments. The vapor phase process might permit application of reagents difficult to apply in solution because of their volatility. The spray method might permit the achievement of unusual one-side effects and of higher production rates.

Drying and curing. In the conventional methods of drying and curing, fabric travel speed is limited by the rate at which water can migrate to the surface for evaporation. In curing, it often happens that the outer parts of the fabric are overdried before the inside is cured. Methods which permit rapid water removal, such as high-frequency curing, might permit a higher travel speed without overheating. Rapid water removal may also make it possible to dry and cure simultaneously, to employ volatile compounds which give nonuniform products in the conventional process, to decrease tensile losses due to acid hydrolysis, to dry and cure fiber bats suitable for quilting and upholstery use, to cure garments impregnated with resins or made from fabrics which have been impregnated but not cured, and to cure cotton at an optimum degree of swelling. Radiation from radioactive sources, though known to degrade cellulose, might be useful when applied in small doses to initiate reactions [50, 539].

Yarn and Fabric Construction

The broad effects of many yarn and fabric construction parameters on wrinkle recovery have been determined. Further research is needed to define the relationships involved in quantitative terms. This would permit a rapid evaluation of the suitability of a given construction for creaseproofing and, even more important, it would permit design of constructions especially well suited for such treatments.

The question of the relative importance of resistance to and recovery from deformation should be resolved. Fabrics differing in stiffness should be designed and their wrinkling behavior tested. The test should be performed on both face and back of the fabrics, and in diagonal directions as well as along warp and filling. The results should be correlated with the various construction parameters, including yarn twist; particular attention should be paid to the effect of the latter on diagonal wrinkling. The study of the effects of various construction parameters should be performed on dry-cured and wet-cured fabrics, and their behavior both wet and dry should be investigated. Water may be expected to swell the fibers. In densely woven fabrics they will have less mobility, and the whole structure may become more rigid. However, water may also lubricate fiber surfaces, and this may lead to greater mobility and less stiffness, particularly in loosely woven fabrics.

It has been suggested that the curling properties of fabrics affect their wrinkling behavior and that an investigation of factors involved in fabric curling is of fundamental importance in the development of optimum construction for wrinkle-resistant cotton fabrics [300].

Perhaps the most important immediate need in this area, however, is for development work rather than basic research. There is a great need to apply what is already known about the effect of construction factors on wrinkle recovery to the design and manufacture of fabrics which do not differ too much in appearance from the traditional constructions. It is known that sateens perform better than broadcloth, for example, but a white business shirt in sateen construction is not acceptable to the trade. It is necessary, therefore, to determine how a standard construction, whose usage for wash-wear items is dictated by custom, can be modified to give optimum wash-wear performance and maximum utility without at the same time changing its appearance so much that it would affect its marketability.

Testing

The subjective panel-type testing methods for wash-wear cottons appear to be reproducible, and the results correlate fairly well with performance in use. Both the preparation of samples for testing and the evaluating procedures, however, are time-consuming and cumbersome. Simplification and standardization of washing methods, lighting conditions, and other parameters of the test would permit

more rapid testing. Objective tests, which measure the mechanical properties of the fabric, their smoothness, and light reflectance also need to be developed further. The relation between wet and dry wrinkle recovery on the one hand, and actual performance in wear and laundering on the other, should be determined quantitatively [676]. Wash-and-wear tests require much time and effort. The development of simple, accurate, and reproducible tests capable of predicting the wrinkling behavior of fabrics in wear and in laundering is a highly desirable research objective.

Durable Creases

Conventional wrinkle-resistant cotton fabrics shed wrinkles and maintain the flat state in which they were cured. By the same token, however, their creaseability is poor and they do not "hold" inserted creases. This hinders the use of wrinkle-resistant cottons in dress trousers and other apparel items which can be given a crease only after they are made up. Cotton fabrics suitable for such products are readily available, and if the problem of durable creasing were resolved, cotton could capture a large part of the market. Some work on this problem has been performed, but the large size of the potential market warrants further efforts.

Garment treatment. One suggested solution consists of applying the treating formulation to finished garments rather than to fabrics [86, 282, 283, 343, 346, 578, 579, 775]. The desired creases are ironed in, and the ironing results in a partial cure. Curing is completed in hot-air cabinets. This method offers the additional advantage of freedom from seam pucker, which often detracts from the appearance of garments sewn from wrinkle-resistant fabrics. Garment treatment has been pronounced feasible both technically and economically, but it has not found, so far, commercial application.

The delayed-cure method. There is a possibility that, in the absence of catalysts, little or no reaction takes place between cellulose and certain cross-linking agents. It might be possible, using such agents, to impregnate and dry the fabric; manufacture garments from it; insert creases in the garment where desired; and then cure the finished product. Some of the amine salts obtained by reacting tertiary amines with alkyl dichlorides are stable at room temperatures and dissociate at elevated temperatures. Compounds of this type should be studied for use in delayed curing.

It may also be possible to develop a catalytic system which would prevent the cross-linking reaction from taking place until triggered by some energizing mechanism, such as heat or high energy radiation. Catalysts claimed to be completely stable below curing temperatures have been described, and these could be utilized in such systems. With more active catalysts it may be possible to stabilize the system by incorporating small amounts of buffering agents to counteract the effect of the catalysts. These would impart stability only for a limited time, but this would be sufficient for some purposes. Stability for longer periods of time might be obtained through the use of larger amounts of inhibitors capable of preventing the reaction at room temperatures, but losing this power through volatilization or disintegration at cure temperatures. It has also been suggested that fabrics be first treated with stable creaseproofing compounds, made into garments, and the finished products cured by application of catalysts in steam [767] or in vapor phase.

Because of the frequent need for alterations in retail merchandising of dress apparel, the delayed cure method would be most useful in the production of work clothes.

The re-curing method. A still different method of introducing durable creases into wrinkle resistant cotton garments depends on treating the area of the fabric to be creased with a solution capable of hydrolyzing cross-linkages [578, 581]. The fabric is then creased by ironing, and cross-linkages are re-formed in the treated area as it is dried and heated by the iron. The hydrolyzing solution may comprise cross-linking agents and catalysts.

Creases formed in this manner are sharper and more durable than those which can be formed by ironing alone. However, they are generally not as strong and durable as those that have been inserted during the original treatment, particularly if the finish was well cured. It appears that not all the cross-linkages in the treated area are hydrolyzed and not all hydrolyzed linkages are reformed. Further development work on this idea is desirable.

A somewhat similar method for inserting creases in wrinkle-resistant fabrics depends on the use of strong caustic solutions [571]. The fabric area to be treated is swollen with caustic and the crease is then pressed in. The crease is durable, but dis-

coloration in the treated area is likely to occur. This method, too, needs further evaluation and development work.

A durable crease can also be introduced into a wash-wear cotton garment by inserting a strip of a thermoplastic material along the crease line on the reverse side of the fabric and then ironing the crease in with heat and pressure. However, abrasion at the crease is a problem.

New Products

Lofty, warm cottons. Experimental fabrics made from fibers creaseproofed in the raw stock form exhibit little wrinkle resistance. However, they are thicker and loftier than fabrics of the same nominal construction made from untreated fibers. Moreover, such fabrics maintain their loftiness in laundering. Since the thermal insulation value of fabrics depends primarily on thickness, durably lofty cotton fabrics could be used for winter apparel, in which low weight and durable bulk are important.

Spinning yarns from treated raw stock, however, is difficult. Aqueous creaseproofing mats the fibers. The mat must be opened and the fibers carded and spun into yarn. These common manufacturing processes are difficult to perform on the treated fibers, and extensive fiber breakage takes place. It has been suggested, therefore, to process treated stock on the woolen system, in which the fibers are not parallelized as highly as in the cotton system. Blending of treated with untreated fibers has been shown to alleviate some of the difficulties encountered in spinning. Development of ways to treat raw stock so that the fibers would not mat would be an important achievement.

It may also be possible to produce a lofty cotton fabric by treating yarns rather than the raw stock. The treated yarns may be back-twisted or plied after curing. Treating of false-twist yarns followed by twisting is another possibility. Various twisting and back-twisting ratios should be investigated to discover those giving the optimum durable bulk.

The possibility of preparing lofty cotton fabrics by treatment applied to the fabric rather than to fibers or yarns should also be investigated. The squeezing step of the conventional creaseproofing process flattens the fabric and decreases its bulk. Tension is normally applied in drying and curing, and the original fabric bulk is not restored. If a fabric were cured without tension, so that fibers and yarns were in continuous motion, free to shrink, they might recover their original crimp. The fabric would thus be cured in a bulky, lofty state. Such an effect might be attainable by curing in machines resembling tumble dryers, in which the fabric would be continuously agitated.

Stretchable cottons. The methods suggested for preparing lofty cottons may be used to prepare yarns for making elastic cotton products, such as stretch socks. A cotton yarn could be set by the treatment in the given twist; upon back-twisting the tendency of the fibers to maintain the configuration in which they are cross-linked will make the yarn bulky and highly extensible. Such yarns could be knit or woven into extensible fabrics if stretching the yarns in the process could be minimized.

Resilient cotton batting. Cotton batting used as cushioning in mattresses and furniture needs improvement in its ability to maintain original bulk. For use as stuffing in quilts and comforters, the batting should also have a better bulk-to-weight ratio, should dry faster, and should not mat on laundering.

The ability to recover from repeated compression and to maintain bulk depends on fiber resilience and bat construction. Treatment with creaseproofing reagents may lead to the development of improved bats. A concurrent improvement in fiber-to-fiber cohesion may be obtained by including in the treating formulation polymeric bonding agents at various stages of condensation. Formaldehyde and the low-polymer fraction of the precondensate would cross-link the fibers, while the high polymer fraction would serve as a binder for the fibers, lowering the extent of fiber slippage in the batting.

Another process which may give beneficial results depends on the incorporation of a thermoplastic material in the batting. The batting could be treated with cross-linking compounds and subjected to elevated temperatures, which would cure the cross-linking compounds on the cotton and at the same time melt the thermoplastic, thus bonding fibers to each other. The bat could be cured in a mold and thus be given any desired shape. The preparation of preformed batting is important for the furniture trade.

Cotton rugs. In cotton cut-pile carpets the ends of yarns forming the pile open up, and this gives the carpet a matted appearance. Treatment with creaseproofing compounds, in addition to making

the yarns more resilient, might also stabilize their twist, thus preventing yarn ends from opening and so decreasing matting. The treatment could be applied to the carpet yarns prior to sewing them onto the backing [2]. It could also be applied by spraying the cut pile using high frequency for drying and curing.

Special products. Creaseproofing processes should be considered as possible means for producing cotton products whose utility for a particular use does not depend on recovery from deformation. Cross-linked cotton cellulose can be more extensively substituted because cross-linking decreases solubility. The use of treated mats or fabrics in lamination might result in improved products. The use of epoxide or phenolic resins might permit cross-linking and laminating in one step.

It may be possible to utilize the resistance to microorganisms and the increased strength of fabrics cured under tension in one product. The three major requirements for an irrigation hose reinforcement are low elongation, high filling-to-warp strength ratio, and mildew and rot resistance. A properly constructed cotton fabric, treated with a formulation comprising cross-linking compounds and weatherproofing agents, cured while under tension in the filling direction only, may well meet these requirements. The acid colloids of resin precondensates may be particularly well suited for this purpose.

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Response of Cottons to Chemical Treatments

Part II: Yarn Mercerization

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Abstract

Eleven experimental cottons were subjected to identical yarn mercerization in an attempt to determine whether differences in response to the treatment could be observed. The response was measured in terms of changes in yarn resilience, elastic modulus, and toughness. Changes in yarn elastic modulus and resilience were found to be dependent upon X-ray angle, although the dependence on X-ray angle was found to be the reverse of that for fiber elastic modulus [6].

Introduction

In Part I of this series experiments were described which were designed to determine whether cottons responded differently to chemical treatments [6]. In that work it was shown that, when six cottons with widely divergent fiber structural characteristics were subjected to mercerization and other swelling-type treatments, the response to the treatment was not constant for the six cottons. The response, as measured in terms of changes in fiber mechanical properties, was dependent upon fibrillar orientation as estimated by the X-ray angle. Such a dependence on the fiber's structure was particularly significant for fiber mechanical properties which are a function of the entire fiber, i.e., breaking extension and elastic modulus. The chemical treatments were performed on single cotton fibers and the response evaluated in terms of changes in single fiber mechanical properties.

This publication deals with the mercerization of yarns and is an attempt to determine whether the response differences which were observed in single fiber mercerization are also evident in yarn mercerization. Particular attention was given to the changes in yarn properties in the low-strain region of the yarn stress–strain curve.

In the mercerization of cotton yarns careful attention must be given to two factors in addition to the usual variables of alkali concentration, temperature, and time of treatment. The tension on the yarn during the treatment is a highly significant factor since the changes in yarn properties resulting from the treatment are highly dependent upon tension [3]. The variable of yarn twist is also important in terms of reagent penetration into the yarn structure and in view of its effect on the dimensional changes which the fibers undergo during mercerization [1].

In this work neither tension nor yarn twist were directly controlled. The experimental yarns were spun at optimum twist multiplier for their particular fiber characteristics. The tension during the treatment was allowed to vary for the several cottons in a complex manner dictated by the swelling forces since the experiments were conducted at constant length conditions. To this extent the experimental conditions differ from the single fiber mercerization treatments, where tension was maintained constant and length was permitted to vary [6].

Experimental

Eleven cottons were used in these experiments. These were made available through the courtesy of the Agricultural Research Service, U. S. Department of Agriculture, in the form 22 singles yarn (26.8 tex). The cottons were chosen on the basis of their divergent fiber characteristics, some of which are listed in Table I. In choosing these cottons, particular attention was given to fibrillar orientation as estimated by X-ray angle, since this fiber structural characteristic has proved to be of such importance in terms of fiber mechanical properties [5, 7]. The yarns were spun at optimum twist at the USDA Spinning Laboratory in Knoxville, Tennessee [4].

TABLE I. Experimental Cottons

No.	Cotton designation	Yarn twist mult.	Array Method		X-ray angle, raw bundle, degrees
			Mean length, in.	Fineness, μg./in.	
3	THEF 96	3.73	0.96	3.6	26.2
5	Hopi Acala	3.73	1.02	4.0	26.3
6	Acala 4-42(B)	3.80	0.97	3.8	29.6
11	Coastland RNET	3.66	1.20	4.6	35.0
21	CR 4	4.26	0.83	4.8	27.7
36	Paymaster 54	3.87	0.93	4.0	39.6
37	Pima S-1	3.66	1.17	3.3	31.8
38	Amsak	3.66	1.28	3.1	30.8
41	Acala 4-42(S)	3.73	1.00	4.0	33.7
49	Smooth Leaf	3.94	0.93	4.8	41.8
55	Lengupa 1954	4.44	0.84	6.4	39.0

Miniature skeins of each of the cottons were prepared on a specially constructed stainless steel frame where it was possible to introduce a restraining tensile force by adjusting the frame dimensions. These dimensions were then maintained throughout the treatment procedure. While it was not possible to evaluate readily the magnitude of the restraining tensile force, the cottons were treated under identical initial yarn length conditions and thus any variation in tension which took place during the treatment can be considered to be a function of the cotton.

The miniature skeins were subjected to a mercerization treatment consisting of immersion for 5 min. in a 25% (by weight) sodium hydroxide solution at room temperature containing a suitable wetting agent to facilitate reagent penetration. The skeins were subsequently washed with tap water, soured in a 1% acetic acid solution, and again thoroughly washed in distilled water. After a 10-min. air drying, the skeins were dried in a forced air oven for 5 min. at 105° C.

The yarn samples were removed from the frame and allowed to condition at 70° F. and 65% RH for at least 24 hr. prior to mechanical testing.

For the untreated condition, similar miniature skeins were prepared but were not subjected to the mercerization sequence. This was done in an attempt to duplicate the mechanical handling of the yarn samples.

Yarn mechanical properties of the mercerized and untreated samples were evaluated on the Instron tensile tester at a 10-cm. gauge length. A single-strand testing method was used and twenty specimens were tested for each condition. In order to characterize the low-strain region of the stress–strain curve, each specimen was loaded to a 150-g. force level at a constant rate of extension of 12%/min. When the 150-g. force level was attained, the cross-head of the Instron was reversed and the test specimen unloaded to a zero force level.

With no relaxation time other than that afforded by the time required to readjust the testing instrument, the yarn specimen was subjected to the second loading cycle, which was carried to the rupture point. The yarn linear density was evaluated by direct weight measurement of the test specimen.

The yarn elastic modulus was determined from the first loading cycle by measurement of the slope of the stress–strain curve and normalization of this value by the yarn linear density. A resilience term was evaluated by comparing the areas under the loading and unloading portions of the first cycle.[1] This factor then conforms to the definition of resilience as the ratio of the energy of retraction to the energy of deformation [2]. This term is further qualified as the resilience from a 150-g. force level. The breaking load and breaking extension were evaluated from the second loading cycle and were used to calculate the yarn toughness. Yarn toughness is defined as one-half the product of breaking tenacity and breaking extension. To the extent that a yarn stress–strain curve is linear over its entire region, yarn toughness is a measure of the rupture energy or the ability of a yarn to absorb energy prior to rupture.

Results

The response of the eleven experimental cottons to the yarn mercerization treatment described above is considered in terms of changes in yarn elastic modulus, resilience, and toughness.

In Table II are shown the values of yarn resilience measured from a 150-g. loading in the untreated and mercerized condition. The relative change in this property resulting from the mercerization treatment is also listed in Table II. A small, yet significant, increase in yarn resilience is the result of yarn mercerization for several of the experimental cottons. The change in yarn resilience is not constant for the experimental cottons but exhibits a statistically significant dependence upon X-ray angle, as indicated in Figure 1. Cottons with low X-ray angles (high orientation) have a higher relative

[1] The areas under these two portions of the stress-strain curve were not actually measured; an estimate of these areas was made by a unidimensional measurement along the strain axis.

increase in yarn resilience than do cottons with a high X-ray angle.

A similar situation exists in the case of yarn stiffness as estimated by the elastic modulus. The result of mercerization under the treatment conditions described above is to increase the elastic modulus for most of the cottons. This increase in elastic modulus is significant, as noted in Table III. The increase in this yarn property is again not constant for the experimental cottons but exhibits a statistically significant dependence upon X-ray angle, as shown in Figure 2. Cottons with low X-ray angle increase their yarn elastic modulus to a greater extent than do cottons with a high X-ray angle.

In Table IV are shown yarn toughness values for the original yarns and for the mercerized yarns. In most cases the mercerization treatment does not significantly affect yarn toughness. Yarn toughness is directly proportional to the breaking tenacity and breaking extension, and an increase in one of these may be offset by a decrease in the other. A 10% increase in yarn breaking tenacity is compensated for by a 14% reduction in yarn breaking extension, considering average values for the eleven cottons. Thus, the fact that yarn toughness is not significantly affected by mercerization does not indicate that mercerization has no effect on rupture properties. In those cases where there was an appreciable change in yarn toughness it could not be related to X-ray angle or to any other known fiber structural characteristic.

TABLE II. Yarn Resilience 150, %

Cotton	Original	Mercerized	Change, %
3	33.7	36.0	+ 7.0
5	33.7	37.7	+12.0
6	35.5	36.8	+ 3.8
11	32.0	33.5	+ 4.7
21	29.8	31.9	+ 7.0
36	30.6	29.0	− 5.2
37	34.8	34.9	+ 0.2
38	34.5	37.8	+ 9.6
41	29.1	32.2	+10.7
49	26.0	25.8	− 0.7
55	24.1	25.5	+ 5.9
Pooled 95% conf. limits	1.5	1.4	

TABLE III. Yarn Elastic Modulus, g./tex

Cotton	Original	Mercerized	Change, %
3	322	391	+21.4
5	347	435	+25.2
6	322	388	+20.2
11	265	291	+ 9.7
21	242	283	+17.0
36	207	212	+ 2.3
37	305	338	+11.0
38	309	358	+16.0
41	233	296	+27.0
49	191	181	− 7.5
55	164	176	+ 7.2
Pooled 95% conf. limits	13	14	

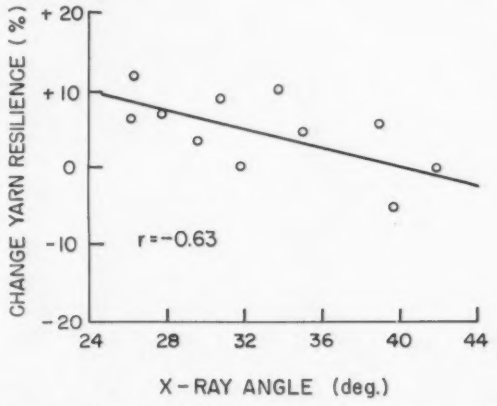

Fig. 1. Relative change resulting from mercerization in yarn resilience measured from a 150-g. loading as a function of raw cotton X-ray angle. The relationship is statistically significant above the 95% confidence level.

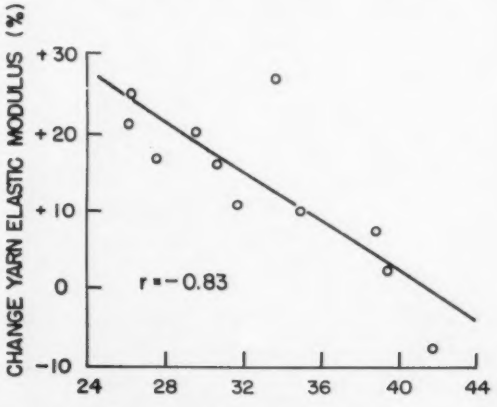

Fig. 2. Relative change resulting from mercerization in yarn elastic modulus as a function of raw cotton X-ray angle. The relationship is statistically significant above the 99% confidence level.

TABLE IV. Yarn Toughness, g./tex

Cotton	Original	Mercerized	Change, %
3	0.454	0.437	− 3.8
5	0.545	0.604	+10.8
6	0.544	0.398	−26.8
11	0.478	0.436	− 8.7
21	0.252	0.267	+ 6.0
36	0.459	0.440	− 4.0
37	0.661	0.630	− 4.6
38	0.797	0.572	−28.2
41	0.385	0.439	+14.0
49	0.371	0.288	+22.4
55	0.349	0.365	− 4.5
Pooled 95% conf. limits	0.050	0.045	

Discussion

Of particular interest is the effect of yarn mercerization on resilience and elastic modulus. Cottons with a low X-ray angle (high orientation) have larger relative increases in yarn elastic modulus and resilience than do cottons with a high X-ray angle. In the case of single fiber mercerization, cottons with high X-ray angles show a greater relative increase in single fiber elastic modulus than do cottons with a low X-ray angle [6]. It must also be noted that fiber elastic modulus values are increased by about 300%, while yarn elastic modulus values are increased by only 10–20%.

The difference in the magnitude of increases in fiber and yarn elastic moduli may be accounted for by consideration of the tension direction during the treatment. In single-fiber mercerization the tension on each fiber is parallel to the fiber axis, whereas in yarn mercerization the tension, which is parallel to the yarn axis, is not parallel to the fiber axis due to yarn twist.

The reason for the reverse dependence on X-ray angle between fiber and yarn mercerization may be found in the fundamental difference in experimental conditions in the two experiments. The single fibers were treated under a constant tensile force, and changes in dimensional and mechanical fiber properties resulting from the treatment are primarily a function of the fiber fine structure. The yarns were treated under constant-length conditions, and the changes in yarn properties are not only a function of the fiber fine structure but also of the changes in yarn construction which take place during the treatment. In yarn mercerization, the changes in fiber cross-sectional and longitudinal dimensions depend greatly on yarn twist and tension; conversely, yarn twist and tension are greatly dependent upon the swelling forces which develop during the mercerization. In yarn mercerization, the different cottons may develop varying tensions as well as varying changes in yarn twist.

While it may therefore be argued that the changes in yarn mechanical properties are not strictly comparable, one must consider all these factors (cotton fiber fine structure, twist, and developed tension) as parts of the over-all variable being investigated: the cotton. The changes in yarn twist and the varying tensions which may develop during constant-length yarn mercerization experiments are in fact reflections of the cottons' response characteristics. Thus the fundamental difference between the single-fiber and yarn mercerization experiments is that in the fiber treatments the changes in properties reflect only the changes in fiber fine structure, whereas in yarn treatments the changes in yarn properties reflect changes in fiber fine structure and in yarn constructional characteristics as well.

Conclusions

The experiments reported in this paper indicate that when different cottons are subjected to yarn mercerization under constant-length conditions, the cottons respond differently. Some of the response differences have been related to cotton fiber structure, particularly fibrillar orientation as estimated by X-ray angle. In view of the complex constructional features of spun yarns, these experiments further indicate that great caution must be exercised in extrapolating information gained from single-fiber experiments to yarns and presumably also to fabrics.

Acknowledgment

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The Reactivity of Some Epoxides toward Cellulose[1]

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Abstract

The reactivity of 25 mono- and diepoxides towards cellulose under hot, anhydrous, acidic conditions has been investigated using a small scale procedure which permits the study of reagents available only in small amounts. The epoxides were emulsified in aqueous solutions of zinc perchlorate catalyst and applied to cellulose in the form of a small piece of cotton fabric. The impregnated sample was then heated at an elevated temperature. The extent of reaction was followed by changes in the density of the cellulose fibers, in their solubility in cuprammonium hydroxide, and in the crease recovery of the fabric. The latter two criteria were important only with difunctional reagents.

The compounds tested were principally aliphatic and alicyclic epoxides in the molecular weight range of 70 to 300. The results suggest that to be able to react with cellulose under these conditions, the epoxide must be non-volatile, water-soluble to some degree, and free from steric hindrance of certain sorts.

THE cross-linking of cellulose with polyfunctional epoxides to impart dimensional stability and resilience was disclosed in the patent literature a few years ago [2, 3, 11, 13]. The durability of the treatment and its freedom from the susceptibility to damage in chlorine bleaching shown by most of the usual nitrogenous finishes made it of considerable interest for fabric finishing. Some commercial exploration and development has been carried out with a product which appears to be a "saturated polyglycidyl ether of a polyhydroxy alcohol having an epoxy equivalent greater than 1.0" [2, 11]. The conclusion from this work seems to be that the maximum practical effect attainable is not quite sufficient to produce good wash-wear behavior in cotton fabrics and that a rather large amount of the reagent is required [14]. It is possible that these shortcomings might be overcome with a product of higher functionality and greater reactivity. We have therefore studied the reactivity towards cellulose of a number of non-polymeric epoxides under the hot, anhydrous, acidic conditions frequently used in the chemical finishing industry. Not all epoxide groups are equally reactive under these conditions and we have sought to discover what factors are important in determining reactivity.

[1] Presented at the Delaware Valley Regional Meeting of the American Chemical Society, Philadelphia, Pa., February 25, 1960.

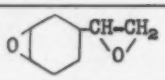
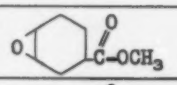
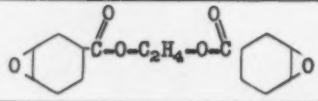
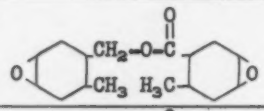
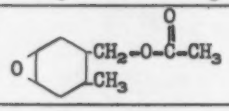
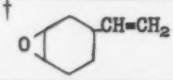
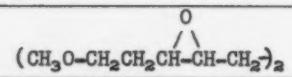
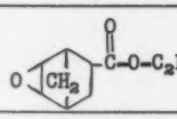
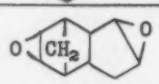
Experimental

The following semi-micro evaluation procedure was used. Two milliliters of a solution containing 1.5% $Zn(ClO_4)_2$ and 0.25% of a nonionic emulsifying agent (Triton X-100) was placed in a small test tube. The desired weight of epoxide was added with a dropper and emulsified by shaking the tube. A milliliter of the mixture was removed in a pipette and applied to a 2×4-in. sample of cotton printcloth weighing $0.82 \pm .02$ g. The swatch was then placed in an oven at 150° C. for 15 min.

The principal criterion used to determine the degree of reaction was the reduction in fiber density, as determined in a density gradient column [7, 12].

To give convenient and easily compared figures, the density change is expressed as 1000 times the difference between the densities of the treated and untreated samples ($\Delta\rho \times 10^3$). Reduction in density is considered a positive effect and is therefore given this sign. The effect of catalyst alone is to give a small increase in density (negative effect). With difunctional compounds the warp crease recovery and the cuprammonium solubility of the treated samples were also determined.

TABLE I. Reactivity of Epoxides toward Cellulose: Compounds Having One Hydrogen on Each Carbon of the Epoxide Group

Epoxide					$\Delta\rho$	Cuoxam	C.R.,
Structure	Source	b. p.	H_2O soly.	Conc.*	$\times 10^3$	soly.	deg.
a.	Exp.	~130° 760 mm.		~20 ~40	-4.4 -3.2	sol. "	86 85
b. 	UCC	227° 760 mm.	18.3%	3.5 7.0 10.5	5.4 38.6 50.1	insol. " "	112 133 135
c. 	Exp.	>110° 10 mm.	0.8%	11.9 23.8	7.5 14.2	sol. "	- -
d. 	Exp.			~10 ~20	7.1 5.6	sol. "	80 74
e. 	UCC	>150° 10 mm.	0.3%	11.3 22.6	17.6 14.1	insol. "	82 93
f. 	UCC	259° 760 mm.	0.71%	10.5 21.0	10.0 16.6	sol. "	- -
g.	UCC	244.5° 760 mm.	4.69%	11.2 22.4	17.2 25.6	sol. "	- -
h.† 	UCC	169° 760 mm.	0.5%	8.2 16.4	-3.9 -3.4	sol. "	- -
i. 	Exp.			10.4 20.8	4.8 13.9	sol. "	82 83
j. 	UCC	255.8° 760 mm.	0.74%	11.1 22.2	1.4 1.9	sol. "	- -
k. 	FMC	130° 10 mm.	insol.	8.3 16.6	3.3 3.6	1/2 sol.	103 101

* Concentration in percent based on fabric weight. Catalyst used was 1.8% $Zn(ClO_4)_2$.
† This was retested with 2.4% $Zn(ClO_4)_2$ or 2.4% $Zn(BF_4)_2$, with no better results.

Compounds Tested and Results

A reasonably wide variety of structures was available.[2] Table I shows a group of compounds characterized by having an epoxy group with one hydrogen atom on each of the epoxide carbons. All but one of these are derivatives of cyclohexene. Cyclohexene oxide itself (Ia) does not react with cellulose under these conditions. The small negative changes in density observed in this case are characteristic of treatment with the catalyst alone. The boiling point of this compound is below the reaction temperature and it probably evaporates before it can react. Vinyl cyclohexene dioxide (Ib) is very reactive, as shown by the substantial change in density. The insolubility of the fabric in cuprammonium hydroxide and its crease recovery indicate that both epoxide groups have reacted so that the cellulose is cross-linked. The boiling point is substantially higher than that of cyclohexene oxide. The crushproofing of cotton fabrics with this compound was discussed in a recent paper [4].

The next two compounds are esters of epoxy cyclohexene carboxylic acid. The methyl ester (Ic) seems to be reactive, but the ethylene glycol diester (Id), which is very insoluble in water, failed to give any evidence of cross-linking. The similar compound next in the table, Ie, is reactive and insolubilized the cellulose, but the low crease recovery indicates that there are not many cross links. The monofunctional cyclohexene oxide derivatives, If and Ig, are relatively reactive and both have high boiling points and appreciable solubility in water. On the other hand, vinyl cyclohexene oxide (Ih) does not react under these conditions, probably because of its volatility.

The straight chain compound, 1,10-dimethoxy-3,4,7,8-diepoxydecane (Ii), produced a fair density change but strangely did not insolubilize the product. The last two compounds are bridged ring structures (Ij, Ik) and show evidence of only a slight degree of reaction.

In general, from study of this first group of compounds, one might conclude that cyclohexene oxide derivatives (without bridges) will react with cellulose under the conditions used if their boiling points are high enough, above 200° C. perhaps being sufficient.

The two epoxide groups in vinyl cyclohexene dioxide are different. The one in the ring is similar to that of the other compounds in Table I. The epoxide group in the side chain has two hydrogen atoms on one of the epoxide carbons and one on the other. Table II shows ten other compounds with epoxide groups of this type. The most reactive of these compounds are the diglycidyl ether of 1, 6-hexanediol (IIa) and decadiene dioxide (IIb). They insolubilize the cellulose and produce relatively large changes in density and crease recovery. The glycidyl ether of dicyclopentadienol epoxide (IIc) also shows some activity at high application levels.

The oxide and dioxide of butadiene (IId, IIe) do not react, probably because of their low boiling points. However, we have found that butadiene dioxide will react with cellulose under hot acidic conditions in a sealed tube.

The comparison of the glycidyl ethers of phenol and isopropanol (IIf, IIg) indicates that the phenyl ether is somewhat more reactive. This difference was rechecked in several experiments and was found even when the reaction was carried out in sealed tubes, indicating that the difference in reactivity was probably not related to the difference in boiling points.

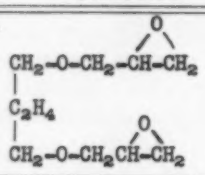
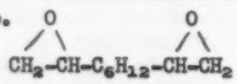
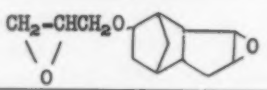
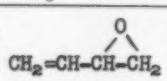
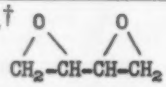
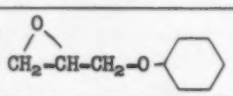
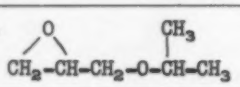
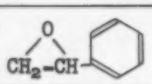
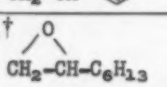
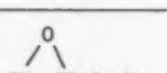
The last three compounds in Table II do not show density changes which would indicate that reaction has occurred. However, with compounds such as the olefin oxides (IIi, IIj) it can be demonstrated that surface reaction has taken place and that a durable water-repellent effect has been imparted to the fabric when the alkyl chain is long enough [10]. The failure to achieve reaction within the fibers with these compounds is probably related to their insolubility in water and the inability of the emulsion droplets to penetrate the fiber. Their largely nonpolar character probably also makes it difficult for the reagent molecules to diffuse into the fiber when they are heated together. We believe that this result demonstrates another requirement that epoxides must meet in order to be reactive under these conditions, that is, that they must have some degree of solubility in water. Inspection of the data presented in Tables I and II indicates that the order of 1% solubility is sufficient. This solubility, measured at 20° C. in distilled water, is necessarily a rather

[2] The source of the materials tested is identified in the tables by the following code: UCC, Union Carbide Chemicals Co.; FMC, Becco Chemical Div., Food Machinery & Chemical Corp.; Ciba, Plastics Div., Ciba Co.; DPI, Distillation Products Industries Div., Eastman Kodak Co.; Dow, Dow Chemical Co.; SCC, Shell Chemical Co.; Exp., experimental preparation.

rough criterion since the penetration of the fiber must actually be determined by the solubility of the reagent at the drying temperature in the catalyst solution. With compound Ie substantial reaction was obtained even though the solubility is only 0.3%. Similarly, Sookne and co-workers [4] found that bis(2,3-epoxycyclopentyl) ether was reactive although its solubility is also only 0.3%.

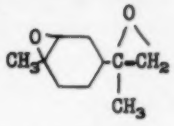
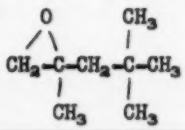
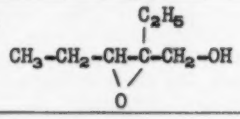
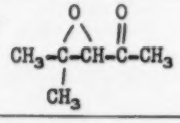
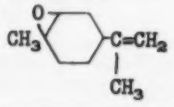
Table III gives the results obtained with two other types of epoxide groups. The first two compounds

TABLE II. Reactivity of Epoxides toward Cellulose: Compounds Having Three Hydrogens on the Epoxide Group

Epoxide					Δρ	Cuoxam	C.R.,
Structure	Source	b. p.	H_2O soly.	Conc.*	× 10^3	soly.	deg.
a. 	Ciba		>2%	10.0 20.0	20.9 40.3	insol. "	115 128
b. 	Exp.	135° .02 mm.	~1%	10.0 20.0	36.5 45.8	insol. "	105 125
c. 	Exp.			~50 ~100	20.1 19.4	insol. "	95 89
d. 	FMC	70° 760 mm.		7.5 15.0	0.2 2.9	sol. "	83 89
e.† 	UCC	138° 760 mm.	∞	10.5 21.0	-5.5 -4.0	sol. "	- -
f. 	DPI	110° 5 mm.	v. low	11.6 23.2	4.4 6.6	sol. "	- -
g. 	DPI	140° 760 mm.	~10%	7.3 14.6	-2.6 -2.6	sol. "	- -
h. 	Dow	194° 760 mm.	0.3%	11.0 22.0	-2.9 1.4	sol. "	- -
i.† 	FMC	72° 27 mm.	v. low	6.6 13.2	-5.4 -4.4	sol. "	- -
j. 	FMC	107° 6 mm.	v. low	7.8 15.6	-3.7 -2.9	sol. "	- -

* Concentration in percent based on fabric weight. Catalyst used was 1.8% $Zn(ClO_4)_2$.
† These were retested with 2.4% $Zn(ClO_4)_2$ or 2.4% $Zn(BF_4)_2$, with no better results.

TABLE III. Reactivity of Epoxides toward Cellulose: Compounds Having Two Hydrogens on One Carbon of the Epoxide Group or Having Only One Hydrogen Substituent on This Group

Epoxide					Δρ	Cuoxam	C.R.,
Structure	Source	b. p.	H_2O soly.	Conc.*	×10³	soly.	deg.
a. 	Exp.	242° 760 mm.	3.2%	2.7 5.4 8.2 16.4 24.6	3.2 12.6 16.7 26.4 25.8	sol. " " " "	90 101 91 93 97
b. 	UCC	141° 760 mm.	0.2%	6.4 12.8	-4.2 -4.7	sol. "	- -
c. 	UCC	131° 50 mm.	0.82%	8.4 16.8	7.2 14.7	sol. "	- -
d. 	SCC	60° 20 mm.	~50%	8.0 16.0	-4.1 -2.8	sol. "	- -
e. 	FMC			6.7 13.4 20.1	-2.6 -1.2 0.5	sol. " "	85 81 81

* Concentration in percent based on fabric weight. Catalyst used was 1.8% $Zn(ClO_4)_2$.

have epoxide groups having two hydrogen atoms on one carbon group and none on the other, while the remaining three have only a single hydrogen substituent on the epoxide group. Dipentene dioxide (IIIa) has two epoxide groups, one of each of these types. At least one of its epoxide groups reacts fairly readily, as shown by the density changes, but the solubility and crease recovery tests show no evidence of cross-linking. We believe that the group external to the ring is the reactive one. A similar group in diisobutylene epoxide (IIIb) did not react, but this compound is both volatile and not very soluble. On the other hand, dipentene oxide (IIIe) did not react.

The lack of reactivity in the ring epoxide of dipentene dioxide is not due simply to the high degree of substitution, since 2-ethyl-2,3,-epoxyhexanol (IIIc) reacts. The non-reactivity of a similarly highly substituted epoxide, mesityl oxide epoxide (IIId), may be due to conjugative or polar effects of the carbonyl group [1, 9] and is not a good comparison. There is not enough evidence available to determine the cause, but the case of dipentene dioxide shows quite clearly that there may be large differences in the reactivity of epoxide groups due to their structure, independent of factors such as volatility or solubility.[3]

[3] The reviewer reports that the ring epoxide in dipentene dioxide hydrolyzes very rapidly in acidic solutions and points out that this could explain the failure of this reagent to be an effective cross-linking reagent. This is a reasonable possibility and should not be neglected.

Discussion

The primary step in the acid-catalyzed reaction of epoxides with cellulose is probably the formation of the conjugate acid of the epoxide:

This is followed by a nucleophilic attack by the cellulose hydroxyl. This may involve preliminary formation of a carbonium ion, as suggested by Pritchard and Long [8] for acid-catalyzed hydrolysis, or the intermediate transition state proposed by Parker and Isaacs [6] in which bond breaking has proceeded to a considerable extent but is not complete.

Under the conditions we have used, the desired reaction probably begins when most of the water has evaporated and the reaction system approaches the temperature of the oven. If considerable water is still present when the conjugate acid begins to react, hydrolysis is likely to interfere with reaction with the cellulose. On the other hand, the conjugate acid, or the carbonium ion formed from it, may be relatively stable, again interfering with the efficiency of the reaction.

What is known of the mechanism of epoxide reactions [6] does not seem to account for the failure of dipentene dioxide to be difunctional with respect to cellulose. The alkali-catalyzed reaction of epoxides with alcohols seems clearly to be an S_N2 reaction and its rate is relatively sensitive to steric factors [5]. However Pritchard and Long [8] have shown that acid-catalyzed hydrolysis can also be affected by such factors and this may be involved in the case of dipentene dioxide.

Conclusion

The conclusions to be drawn from these results, which should be considered tentative until further data are available, would be that in order to be an effective cross-linker for cellulose under the usual resin-finishing conditions for textiles, a difunctional epoxide must also be: moderately water soluble, $\sim 1\%$ or more; relatively non-volatile, b.p. $> 200°$ C.; and free from certain types of steric and polar effects, not well defined as yet, which interfer with the reaction of the epoxide group and the cellulose hydroxyl.

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Fluorescent Brightening Agents: Their Photodecomposition in Aqueous Solution and on Substrate and Phototendering Activity for Cellulose

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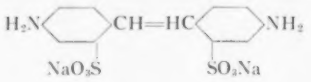
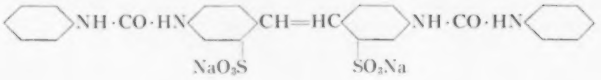
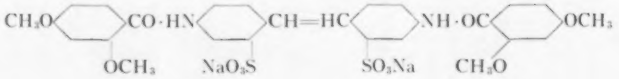
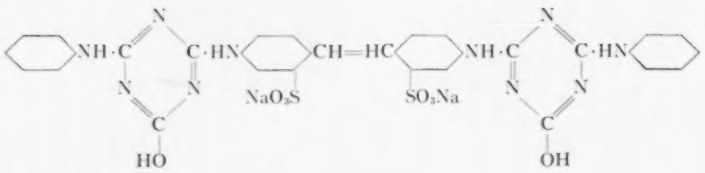
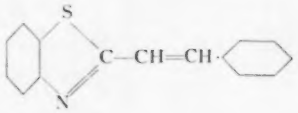
Abstract

Absorption characteristics and fluorescent decay of fluorescent brightening agents derived from 4:4′-diaminostilbene-2:2′-disulfonic acid and of a thiazole derivative when present in aqueous solution and on cellulosic substrate after exposure to sunlight and Fade-Ometer irradiations have been studied. Simultaneous with the decomposition of the brighteners, the bursting strength of the treated fabric decreases after exposure, cuprammonium fluidity increases, and there is a rise in the reducing power of the treated cellulose fiber substance. The extent of degradation of the cellulose depends on the amount of brightener present on the substrate, the type and duration of irradiation and the chemical constitution of the brightener. A correlation has been found to exist between the rate of decomposition of the brightener and the extent of tendering; those compounds which decompose more readily also bring about enhanced tendering. Results also indicate that not only are the parent brightening agents effective for phototendering of cellulose but their photodecomposition products are also responsible for the breakdown of cellulose chain molecules.

Introduction

Textile materials made from natural or synthetic fibers generally show a yellowish tinge due to the presence of certain colored impurities which absorb some of the incident light in the blue region with the result that the fabric does not appear perfectly white. Removal of the yellowish tinge can be achieved by removal or destruction of the coloring matter itself by chemical treatments, addition of bluing agents which absorb the yellow light and thereby bring down the level of light reflected in this region to that of the blue range, or by treatment with certain organic compounds (fluorescent brightening agents) which have the capacity of absorbing light in the ultraviolet region of the spectrum of daylight or artificial light and re-emitting it as light in the blue, red, or green regions of the visible spectrum. Although considerable amount of work has been carried out in the development of fluorescent brightening agents for different fibers [1], on methods for their evaluation in aqueous solutions and on substrate [6, 11, 12, 18], and on methods of application, as well as on the mechanism of adsorption [7, 13], very little is known about the changes in the fiber properties of optically brightened textiles during exposure to ultraviolet irradiation. Graham and Statham [8] showed that appreciable photochemical oxidation of wool took place during irradiation when fluorescent brightening agents were present, and put forward evidence that oxidation of the amino acid tryptophane took place during the exposure. In the present work, photodecomposition and loss in fluorescence on exposure to sunlight and Fade-Ometer arc lamp of brightening agents derived from 4:4′-diaminostilbene-2:2′-disulfonic acid and also of a thiazole derivative when present in aqueous solution and on different cellulosic substrates have been studied. Changes in fiber characteristics, such as reduction in bursting strength, increase in fluidity of the cuprammonium hydroxide solution containing the brightened material, and increase in the reducing power of cellulose have been determined for samples

TABLE I. Fluorescent Brightening Agents and Their Absorption Maxima and Molar Absorptivity

Commercial name	Constitution	Color index: Fluorescent brightening agent no.	Color index: Constitution no.	Molecular weight	λ Maximum, mμ	Molar absorption
—		—	—	414	330	6,820
Blankophor R		30	40600	652	335	21,400
Pontamine White 2GT		34	40605	742	345	16,280
Blankophor B		32	40620	786	340	34,970
Uvitex RS		41	49015	237	360	8,940

treated with different brighteners and exposed for different durations. An attempt has been made to correlate fading behavior with the tendering activity of these compounds for cellulose.

Experimental Materials and Methods

The fluorescent brightening agents used in the present work are shown in Table I.

Purification of the commercial samples of Blankophor R, Pontamine White 2GT, and Blankophor B was carried out by repeated precipitation with sodium acetate from hot aqueous solution followed by extraction of acetate with absolute ethanol, a method similar to that employed by Robinson and Mills [16] for the purification of direct cotton dyes. In the case of 4:4′-diaminostilbene-2:2′-disulfonic acid, the requisite quantity of sodium hydroxide solution was added to the commercial sample so as to convert the sulfonic acid to the sodium salt. This was then dissolved in a limited amount of water. The solution was filtered hot to remove water-insoluble impurities. This procedure was followed by the precipitation treatment with sodium acetate and subsequent extraction with absolute ethanol mentioned above. For the purification of Uvitex RS, the commercial product was precipitated out several times from aqueous solution by controlled additions of absolute ethyl alcohol. The purity of all the compounds was checked by analysis of the elements present. All the brighteners were stored in the dark in a desiccator over P_2O_5.

The sodium chloride used was of Analar quality. In the case of pyridine, pure reagent-grade pyridine was distilled, and the fraction boiling at 112–115° C. was collected and used.

Fiber Substance

Cotton cellulose. Fabric made from 20s single yarn prepared from Indian cotton was used. After careful purification by standard procedure it had the following specifications.

(i) Copper number [9]	0.02
(ii) Fluidity in cuprammonium hydroxide solution (0.5%) [5]	3.8 poises^{-1}
(iii) Carboxyl content as determined by iodometric method [15]	0.724 meq./100 g.

Viscose rayon. Commercial sample of plain taffeta viscose fabric with the following construction was given a mild scouring treatment with 0.5% sodium carbonate and 2% soap for 2 hr. at the boil to remove glycerol and other sizing ingredients present. The fabric was then washed, hydroextracted and dried at 30° C. The warp and weft were 100 den., 40 fil., 1½ twists/in. Reeds were 110/in. and picks were 72/in.

Measurement of Absorption Spectra of Brightener in Aqueous Solution after Exposure to Sunlight and Fade-Ometer Radiation

Equimolar aqueous solutions of brighteners ($18 \cdot 10^{-6}$ moles/l.) were prepared in the dark in amber-colored flasks and were exposed in Pyrex glass stoppered tubes to solar radiation in Bombay during the months of October to May between 10 a.m. and 4 p.m., and to radiation from the "Atlas" Fade-Ometer lamp at $60 \pm 2\%$ RH and $38 \pm 2°$ C. at a fixed distance of 10 in. from the source of light. After exposure, the solutions were allowed to remain for 2 hrs. in the dark to prevent complications arising from cis–trans transformation. The absorption spectra of the solutions were determined on a Beckman DU model spectrophotometer. To determine the extent of decomposition of a brightener after a specific period of exposure, the amount of the original brightening agent remaining in the aqueous solution after exposure was determined from the optical density of the solution measured at a wavelength of maximum absorption in the UV region for the particular compound on the spectrophotometer, which had been previously calibrated with standard solutions of the brightening agent.

Measurement of the Fluorescence Intensity of Aqueous Solutions of Brighteners after Exposure to Sunlight and Fade-Ometer Radiation

Equimolar aqueous solutions of different brightening agents ($18 \cdot 10^{-6}$ moles/l.) were exposed to solar and Fade-Ometer radiations for different periods under the conditions mentioned above. Loss in fluorescence intensity of the exposed solution was determined on a Knett Fluorimeter using the 388 mμ filter and comparing the fluorescence intensity of the irradiated solution with that of an unirradiated solution of the same brighening agent.

Application of Brightening Agents to Different Fiber Substances and Determination of Brightener on Substrate

To achieve uniformity of application, the fabric to be treated was cut into long strips, 1.25 in. wide. The strips were wound over different sections of a stainless steel frame, taking care that overlapping of the fabric did not take place. The frame containing the fabric was inserted into a standard solution of a brightener, contained in a stainless steel vessel. The liquor:material ratio was maintained at 100:1 and the temperature of the liquor was kept constant at $30 \pm 1°$ C. The frame was rotated at a constant speed of 100 r.p.m. After impregnation of the material with the brightener for 10 min., the requisite amount of sodium chloride was added to the liquor for exhaustion. At the end of 1 hr. the frame was removed from the liquor, the fabric rinsed with ice-cold water to remove superfluous brightener solution, squeezed, dried at $30 \pm 1°$ C., and stored in the dark at 65% RH and 30° C. As the uptake of the brightening agent by the fiber substance, when applied by the exhaust method, was low, padding technique was used when higher proportions of the brightener were required on the substrate. In this case, padding was carried out on a two-bowl padding mangle at $30 \pm 1°$ C., keeping the expression at 85%. The fabric was then dried at 30° C. and stored in the dark.

The amount of the brightening agent present on the treated material was determined by estimating the amount of the brightening agent present in the liquor before treatment and the amount present in the exhausted bath and the washings combined. For these estimations, the optical density of a solution was measured on a Beckman DU model spectrophotometer, previously calibrated with standard solutions of the brightening agent, at a wavelength of absorption suitable for the particular brightener.

Conditions of Exposure

Optically brightened fabrics were exposed to solar radiation at an angle of 45° to the horizontal during the months of October to May in Bombay between 10 a.m. and 4 p.m. In the case of Fade-Ometer exposures, samples were mounted on frames attached to the rotating frame of the Fade-Ometer at a fixed distance of 10 in. from the source of irradiation. Both in the case of sunlight and of Fade-Ometer exposures, untreated samples were also exposed as blanks for each specific period of exposure. All the samples were conditioned in the dark for subsequent analysis.

Determination of the Loss of Fluorescence of Brightened Fabrics after Exposure

The fluorescence intensity of fabric treated with a brightener was determined before and after exposure on a Beckman DU model spectrophotometer using a mercury vapor lamp as an external source of illumination and as a modified method of measurement. The choice of a mercury arc as an external source of illumination was inevitable because the intensity of the mercury arc lamp supplied with the spectrophotometer was found to be too low for measurements. In order to obtain high intensity of the incident light, a quartz condensing lens was used between the mercury arc and the entrance slit of the spectrophotometer. The 2580 reflectance attachment was used for measuring the diffused reflectance of the sample relative to the reflectance of the standard material. For better reproducibility, the test sample and the standard reflectance sample were folded into two layers and placed in suitable compartments taking care that the samples were not displaced during measurement; otherwise considerable variation in reflectance was observed. The controls of the spectrophotometer were operated in the usual manner for making reflectance measurements. The angle of the Nicol prism was so adjusted that light falling on the sample was monochromatic with a wavelength of either 313 or 365μ, corresponding to the mercury lines, depending on the type of the brighter studied. The slit width was so arranged as to get a reading of 100 on the scale when the standard sample was in position. The sensitivity indicator was maintained at a position intermediate between maximum and minimum. The exposed sample was then brought into the light path, and the relative reflectance by the sample was measured. Selection of the standard reference sample was difficult because even the untreated cellulosic fabric showed considerable reflectance at 313 and 365 mμ radiation, leading to rather narrow differences in reflectance between the untreated, brightened and unexposed, and brightened and exposed samples. Thomson et al. [19] have also recorded that cotton fabrics show about 25–35% and viscose rayon about 40–60% reflectance in the

300–350 mμ range. In order to make satisfactory arbitrary measurements of fluorescence at these specific wavelengths, the standard sample selected for each brightener was one which contained sufficient optical brightening agent to cover up satisfactorily the reflectance by the fabric. Against such a standard sample for each of the brighteners, the fluorescence-reflectance characteristics of the exposed samples of the corresponding brighteners have been studied.

Determination of Fiber Properties of the Exposed Brightened Samples

Exposed samples to be examined for fiber characteristics, such as bursting strength, fluidity in cuprammonium hydroxide solution, and copper number, were first extracted with 25% aqueous pyridine to remove completely the remainder of the brightener from the fabric as well as decomposition products of the brightening agent. Samples were washed free of pyridine with distilled water, dried at 30±1° C. and stored at 65% RH and 30° C. Blank samples were also similarly treated with aqueous pyridine.

Bursting strength of the conditioned samples was determined on a Goodbrand bursting strength testing machine under standard conditions. A mean of 30 readings was considered for each sample. Fluidity of the standard cuprammonium hydroxide solutions containing the sample was determined by the method recommended by the Fabrics Research Committee of the Department of Scientific and Industrial Research, Great Britain [5]. The reducing power of the fiber substance has been expressed in terms of copper number, determined by the method of Clibbens and Geake as modified by Heyes [9].

Experimental Results and Discussion

Absorption Characteristics of Brighteners in Aqueous Solutions after Exposure

In Table I are given wavelengths of maximum absorption and molar absorptivity for the five fluorescent compounds studied. Introduction of ureido groups in the molecule of diaminostilbenedisulfonic acid does not alter the absorption maxima to an appreciable extent (330 to 335 mμ), but the increase in the resonance system brings about an increase in molar absorptivity from 6,820 to 21,400. In the case of Pontamine White 2GT, the orthomethoxy substituents interfere with the attainment of planar configuration, with the result that there is a hypsochromic shift in the absorption maxima from 335 to 345 mμ and a decrease in molar absorptivity from 21,400 to 16,280. With Blankophor B, the introduction of triazine rings into the molecule brings about noncoplanarity of the molecule to a slight extent only, with the result that the hypsochromic shift is not as great as in the case of Pontamine White 2GT. However, as the resonance area has been increased considerably by the introduction of substituted triazine rings, a considerable increase in molar absorptivity, *viz.* from 6,820 to 34,970, was found to take place. With Uvitex RS, which is a benzthiazole compound, the absorption maxima is at 360 mμ which is the longest absorption wavelength of all the compounds examined, while the molar absorptivity is comparatively low because of the low resonance system. Results on the absorption characteristics of the compounds studied are in fair agreement with those recorded by Heine and Pierce [10] except that the values for molar absorptivity recorded by these workers for each of the compounds are higher, probably due to the high purity grade of the compounds analyzed.

Utraviolet absorption of aqueous solutions of the compounds after irradiation both by sunlight and Fade-Ometer lamp shows two distinct characteristics. In the first instance, the long-wavelength band between 330–345 mμ, which is the main stilbene band, shows a fall in intensity with increasing exposure while at the same time the short-wave band between 235–265 mμ shows a rise in intensity. The UV absorption spectra of the aqueous solutions of Pontamine White 2GT and Blankophor R after different periods of exposure are shown in Figures 1 and 2. Of the compounds studied, only 4:4′-diaminostilbene-2:2′-disulfonic acid gives colored decomposition products, and aqueous solutions of this compound turn yellowish brown on exposure. This may be attributed to cis–trans transformation, as observed by Lewis et al. [14] for stilbene, which turned yellow on exposure. With progressive exposure, unstable intermediate compounds are formed which show an increase in absorbency in the 235–265 mμ band. With Blankophor R and Pontamine White 2GT, there is a marked increase in absorbency in this band during the initial stages of Fade-Ometer exposure, followed by a decrease in absorption when the time of exposure is extended

further (Figures 1 and 2). The maximum yield of these intermediate decomposition products for Fade-Ometer exposure is found in the case of Blankophor R to occur after about 20 hr. and in the case of Pontamine White 2GT after 40 hr. With all the compounds studied, changes brought about in absorption in the 220 mμ band during exposure are not appreciable. Comparison of sunlight and Fade-Ometer exposures indicates that the trend of the changes in absorption spectra during both kinds of irradiation is the same except that the reduction in intensity of the 330–345 mμ waveband and the increase in the 230–265μ band is more marked in the case of Fade-Ometer exposure than in the case of solar exposure of the same duration, due to the differences in the spectral distribution of the two sources of irradiation. Similarly, the production of colored decomposition products in the case of diaminostilbenedisulfonic acid is more pronounced during exposure to the Fade-Ometer lamp than during solar irradiation.

The extent of decomposition for each specific period of exposure to sunlight and to Fade-Ometer-lamp radiation, for the five compounds studied, is maximum during the first 15 hr. of Fade-Ometer exposure and during about 30 hr. of solar exposure. Results of the extent of decomposition for different Fade-Ometer exposures are plotted in Figure 3. It can be seen that the extent of decomposition in the case of Blankophor R and diaminostilbenedisulfonic acid decreases rapidly after 15 hr. of exposure, and after 30 hr. there is no further decomposition even when the period is increased to 80 hr. In the case of Pontamine White 2GT, Uvitex RS, and Blankophor B, however, no indication is given of the decomposition coming to a standstill even after 80 hr. exposure. The order of the extent of decomposition during the first 15 hr. for the different compounds is as follows: Blankophor B < Uvitex RS < diaminostilbenedisulfonic acid < Pontamine White

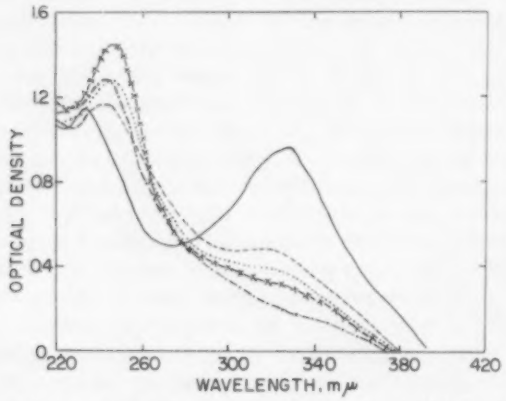


Fig. 1. Absorption spectra of aqueous solutions of Blankophor R after exposure in Fade-Ometer. ——— unexposed; – – – exposure time 10 hr.; · · · exposure time 20 hr.; -x-x-x exposure time 40 hr.; -·-·-· exposure time 80 hr.

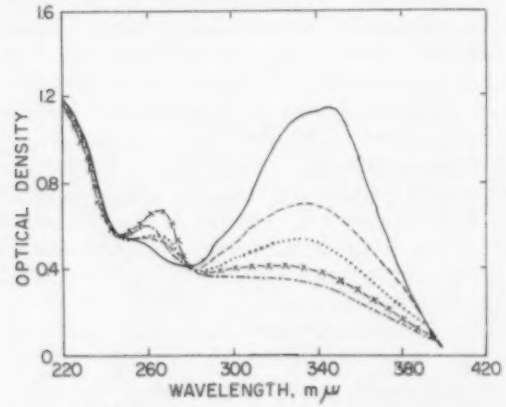


Fig. 2. Absorption spectra of aqueous solutions of Pontamine White 2GT after exposure in Fade-Ometer. ——— unexposed; – – – exposure time 10 hr.; · · · exposure time 20 hr.; -x-x-x exposure time 40 hr.; -·-·-· exposure time 80 hr.

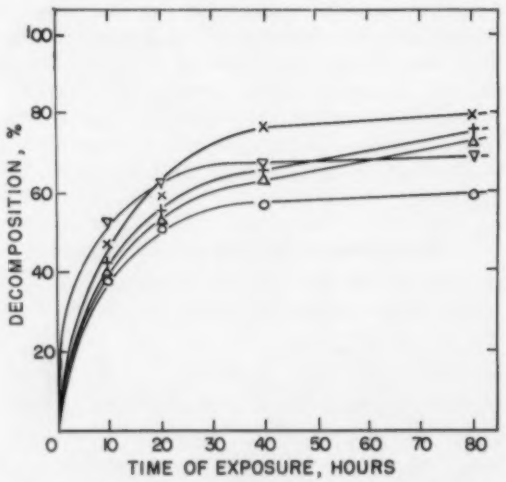


Fig. 3. Decomposition of different brighteners in aqueous solution after exposure in Fade-Ometer. ▽ Blankophor R; × Pontamine White 2GT; + stilbenedisulfonic acid; △ Uvitex RS; ○ Blankophor B.

2GT < Blankophor R. There appears to be no correlation between the extent of decomposition of the brightener and its chemical constitution or molar absorptivity.

During the course of the present work it was also observed that absorbency characteristics of the brighteners studied during irradiation to Fade-Ometer lamp were in general similar whether the brightener was present in aqueous solution or on a transparent viscose sheet.

Change in Fluorescence Intensity of Brighteners in Aqueous Solutions during Exposure to Sunlight and Fade-Ometer Lamp

In the case of Fade-Ometer exposures of all the compounds studied, a sudden decrease in fluorescence intensity takes place during the first 15 hr., followed by a much smaller reduction during the period from 15 to 40 hr.; between 40 and 80 hr. the decrease is considerably lower (Figure 4). During sunlight exposure, the decrease in fluorescence intensity is comparatively less for each specific period of exposure. In this case, loss in fluorescence intensity is rapid during the first 30 hr. of exposure, after which there is a gradual progressive reduction up to 80 hr. (Figure 5). Introduction of substituents in the molecule of diaminostilbenedisulfonic acid improves considerably the resistance to loss in fluorescence during exposure. Dimethoxybenzoyl groups impart maximum resistance, introduction of triazinyl groups shows lower effects, while the effect of the introduction of ureido groups is not very marked. The thiazole compound ranks between the triazinyl and ureido derivatives from the point of view of loss in fluorescence during exposure. Except for diaminostilbenedisulfonic acid, there is a definite relationship between loss in fluorescence capacity of a brightener and reduction in intensity of absorption in the waveband 330–345 mμ during exposure of aqueous solutions of these compounds both to sunlight and to Fade-Ometer lamp radiation. Results for sunlight exposures are plotted in Figure 6. The fluorescing capacity decreases in direct proportion to

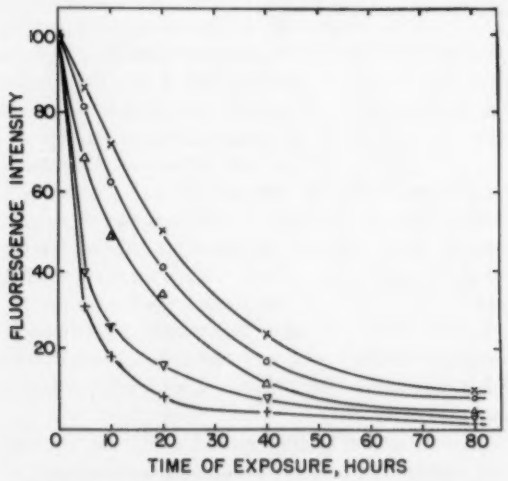


Fig. 4. Loss in fluorescence intensity of aqueous solutions of brighteners after exposure in Fade-Ometer. × Pontamine White 2GT; ○ Blankophor B; △ Uvitex RS; ▽ Blankophor R; + stilbenedisulfonic acid.

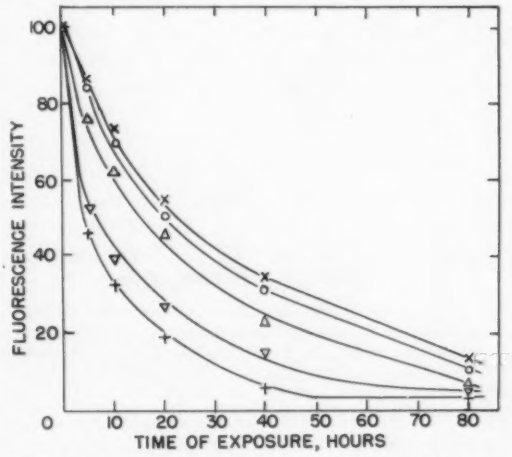


Fig. 5. Loss in fluorescence intensity of aqueous solutions of brighteners after exposure to sunlight. × Pontamine White 2GT; ○ Blankophor B; △ Uvitex RS; ▽ Blankophor R; + stilbenedisulfonic acid.

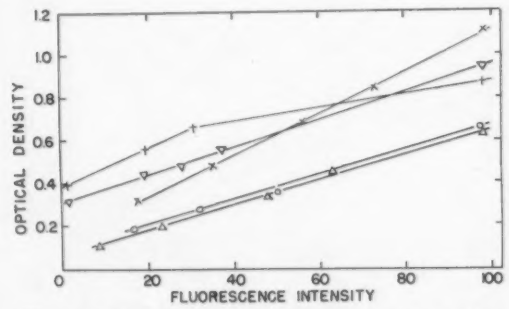


Fig. 6. Relation between fluorescence intensity and optical density of aqueous solutions of brighteners after exposure to sunlight. + stilbenedisulfonic acid; ○ Blankophor B; × Pontamine White 2GT; ▽ Blankophor R; △ Uvitex RS.

the loss in absorption intensity in the 330–345 mμ region. This is in agreement with the fact that the fluorescing capacity of these compounds is mainly due to the stilbene grouping which has an absorption in the 330–350 mμ waveband. The deviation of diaminostilbenedisulfonic acid from other brighteners in this behavior can be attributed to the formation of strongly fluorescent decomposition products after exposure. Decomposition products of this brightener show strong fluorescence in the yellow green region and, although the original violet fluorescence measured with a 338 mμ filter is reduced considerably after exposure, there is a positive rise in fluorescence after exposure when measurements are carried out using a 515 mμ filter. The extent of reduction in fluorescence at each stage of exposure increases in the order: Pontamine White 2GT < Blankophor B < Uvitex RS < Blankophor R < diaminostilbenesulfonic acid, and this order is the same for Fade-Ometer and sunlight exposures. Except for Pontamine White 2GT and diaminostilbenedisulfonic acid, the order of reduction in fluorescence intensity runs parallel with the order of susceptibility to decomposition during irradiation mentioned before.

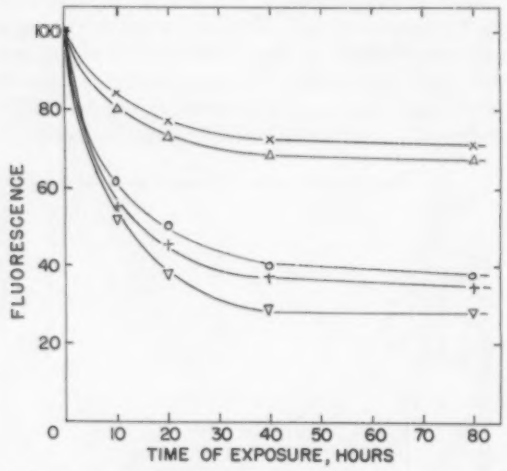


Fig. 7. Loss in fluorescence of cotton cellulose treated with different brighteners after exposure in Fade-Ometer. × Pontamine White 2GT; △ Uvitex RS; ○ Blankophor B; + stilbenedisulfonic acid; ▽ Blankophor R.

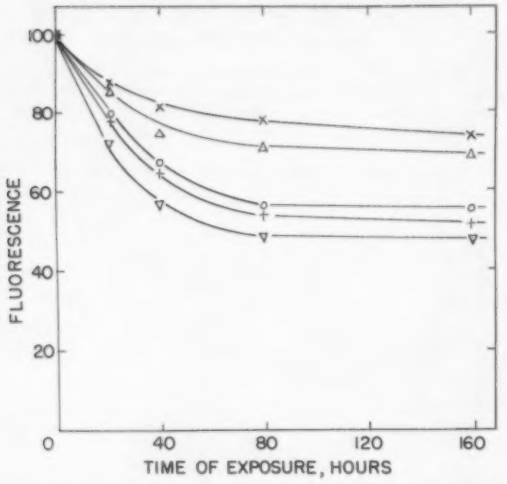


Fig. 8. Loss in fluorescence of cotton cellulose treated with different brighteners after exposure to sunlight. × Pontamine White 2GT; △ Uvitex RS; ○ Blankophor B; + stilbenedisulfonic acid; ▽ Blankophor R.

Changes in Fluorescence Intensity of Brightening Agents on Cellulosic Fiber Substance during Exposure to Sunlight and Fade-Ometer Lamp

As mentioned earlier, the measurement of fluorescence intensity of brighteners on cellulosic substrate presented for several reasons many difficulties. Most of the brightening agents studied show absorption in the region of 330–345 mμ, a wavelength region where cellulosic textiles also show considerable reflectance [19]. In the selection of a standard reference sample for each brightener, it has been assumed that when sufficient amount of the brightener is present on the substrate, the contribution to fluorescence by the brightener is considerably higher than that due to reflectance by the fiber substance and that the latter is more or less masked by the fluorescence of the brightener. Furthermore, with some brighteners the products of photodecomposition are colored. This introduces an additional difficulty in actual measurements because it is not possible to assess how far the colored decomposition products subdue the reflectance by the substrate at this particular wavelength. Thus, the values recorded in the present work for the fluorescence intensity of a brightener on the substrate should be considered empirical and be used only for rough comparison of the fluorescence decay of the brighteners during irradiation.

The reduction in fluorescence of all the brighteners studied on both cotton cellulose and viscose during irradiation by Fade-Ometer lamp is considerable during the first 20 hr. of exposure. This is followed by a progressive decrease up to 40 hr., and from 40

to 80 hr. exposure, there is practically no more change in fluorescence (Figure 7). In the case of exposure to sunlight, rapid decrease in fluorescence on both cotton and viscose takes place during the first 30 hr., lesser reduction between 30 and 80 hr., after which there is no significant loss in fluorescence even when exposure time is extended to 160 hr. (Figure 8). The extent of fluorescence decay after any specific period of sunlight or Fade-Ometer lamp irradiation increases, in the case of both cotton and viscose, in the order: Pontamine White 2GT < Uvitex RS < Blankophor B < diaminostilbenedisulfonic acid < Blankophor R; an order which, except for Blankophor B and diaminostilbenedisulfonic acid, is the same as that recorded earlier for the loss of fluorescence of a brightener when present in aqueous solutions. Investigations on the loss of fluorescence of optical brighteners on wool substrate carried out by Wagle [20] indicate that the rate of fluorescence decay of the brighteners recommended for use on wool are different in aqueous solution and on wool substrate. For instance, Blankophor WT was found to show considerable reduction in fluorescence during exposure when present in aqueous solution, while Blankophor B retained fluorescence for longer times under similar conditions of exposure. On the other hand, when these brighteners were present on wool, fluorescence decay for Blankophor B was more than double that for Blankophor WT.

The only other major work published so far on the loss of fluorescence of a brightening agent on cellulosic fiber substance during exposure is by Elöd and Jörder [4]. It is not possible to compare the results of the present work with those of Elöd and Jörder, because in the present case purified brighteners are used and the amount of the brightener present on the substrate is kept the same for proper comparison, while the latter workers used commercial brands for their investigation and the amount present on the substrate in each case is not indicated. However, the order of fluorescence decay in both these works is nearly the same, *viz.*, Uvitex RS shows maximum resistance, Blankophor B is intermediate in its susceptibility, and Blankophor R fades very rapidly during a short exposure time. In both these investigations, it has been observed that fluorescence decay during exposure to Fade-Ometer is slightly more than double that observed in sunlight exposures of the same duration. There is, however, one point of disagreement between the results of the present work and those of Elöd and Jörder. In the present work it was found that fluorescence decay of all the compounds studied both in the case of Fade-Ometer and solar exposures was nearly the same whether the brightener was present on cotton or viscose, while the latter workers have reported that the brighteners studied by them showed higher fluorescence decay on cotton than on viscose.

Changes in Properties of Cellulosic Fiber Substance Treated with Fluorescent Brighteners after Exposure to Sunlight and Fade-Ometer Lamp

During the present investigation it has been observed that all the brighteners studied bring about progressive tendering of cellulose fiber substance after irradiation, and in each case bursting strength of the irradiated sample decreases considerably (Figures 9 and 10) while the cuprammonium fluidity and the copper number of the exposed samples increase appreciably as compared with untreated samples exposed for the same duration. Results obtained with Blankophor R on cotton cellulose at different brightener content on the substrate are plotted in Figure 11. Increasing the concentration of the brightener on the substrate or the time of exposure enhances the photochemical degradation after both Fade-Ometer irradiation and solar exposures. In Table II are given values for the cuprammonium fluidity of cotton cellulose dyed with purified direct dyes [2] and with commercial vat dyes [17] after exposure to Fade-Ometer lamp and sunlight. These values have been compared with those observed with fluores-

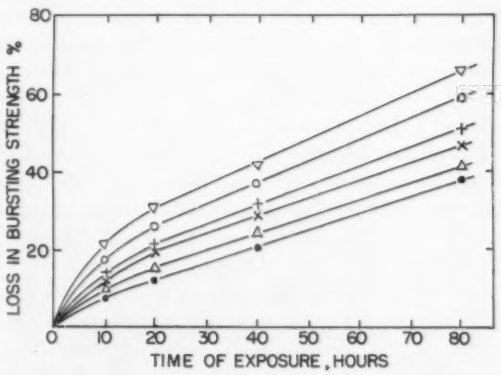


Fig. 9. Loss in bursting strength of cotton cellulose treated with different brighteners after exposure in Fade-Ometer. ▽ Blankophor R; ○ Blankophor B; + stilbenedisulfonic acid; × Pontamine White 2GT; △ Uvitex RS; • untreated.

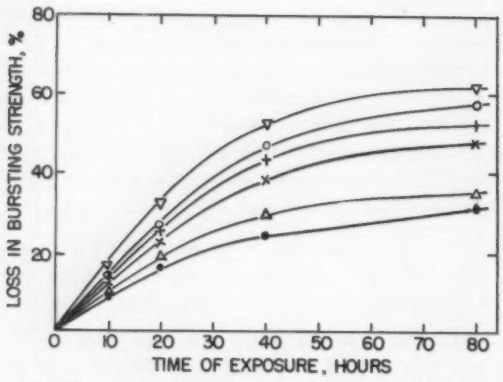


Fig. 10. Loss in bursting strength of viscose fabric treated with different brighteners after exposure in Fade-Ometer. ▽ Blankophor R; ○ Blankophor B; + stilbenedisulfonic acid; × Pontamine White 2GT; △ Uvitex RS; • untreated.

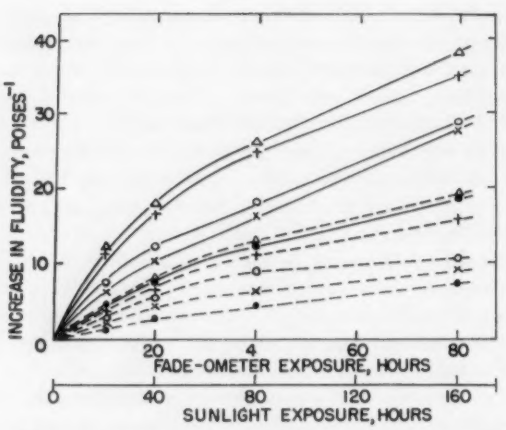


Fig. 11. Increase in fluidity of cotton cellulose containing different amounts of Blankophor R after exposure in Fade-Ometer and sunlight. ——— exposure in Fade-Ometer; – – – exposure to sunlight. △ brightener content 1.0%; + brightener content 0.5%; ○ brightener content 0.15%; × brightener content 0.015%; • untreated.

cent brighteners. The results show that when the amount of the brightener present on the substrate is of the order of 1%, tendering is as great as that for most tendering type of vat dyes, such as Cibanone Yellow R, Cibanone Orange R, Indanthrene Yellow G, etc. When the proportion of the brightener on the substrate is lowered, tendering effect is reduced; but in all cases tendering is higher than that observed for untreated samples irradiated for the same duration.

Relation between rise in fluidity and the amount of brightener present on the substrate at every specific period of exposure is linear for both Fade-Ometer and sunlight exposures. Results of Fade-Ometer exposures are plotted in Figure 12. Furthermore, for the same duration of exposure, the tendering effect, as measured by loss in bursting strength or rise in fluidity, is higher after Fade-Ometer exposure than in the case of sunlight because of the differences in the spectral distribution of the two sources of irradiation, the carbon arc radiations having a higher proportion of wavelengths in the UV than sunlight. Results of bursting-strength measurements also indicate that under any specific set of conditions, such as amount of brightener present on substrate, time of exposure, etc., viscose degradation is slightly less than that of cotton cellulose (Figures 9 and 10). For both the sources of irradiation and for both the fiber substances studied, the order of effectiveness of the presence of fluorescent brightening agents in enhancing photochemical tendering is as follows: Uvitex RS < Pontamine White 2GT < diaminostilbenedisulfonic acid < Blankophor B < Blankophor R. This order, except for Uvitex RS and diaminostilbenedisulfonic acid, runs more or less parallel with the order of increase in fluorescent decay of brighteners mentioned before. Thus, a brightener which shows high fluorescence decay on the substrate during a specific period of exposure is also responsible for greater tendering.

One of the interesting observations recorded in the present work is that not only does photochemical tendering of cellulose take place during the decomposition of the brightener present thereon, but this tendering action still continues with increasing periods of exposure after the brightener has lost its fluorescing capacity (Figures 7, 8 and 11). This goes to show that even the photodecomposition products of the brighteners formed during exposure are responsible for catalyzing the photochemical tendering of the substrate.

The initial process responsible for the production of various effects, such as tendering of fiber substance, fading of a dye or brightener, etc., is the absorption of light by the sensitizing compound. As a result of the absorption of energy, the electrons in the molecule of the sensitizing compound (in the present case the brightener) are raised to a higher energy level. After a very short interval of time, the excited molecule returns to the ground

TABLE II. Fluidity Values of Cotton Cellulose Treated with Direct and Vat Dyes and Brighteners after Exposure to Fade-Ometer Lamp and Sunlight

Name of the compound	Amount present on fiber substance, g./100 g. dry sample	Fade-Ometer exposure			Sunlight exposure		
		Original fluidity, poises^{-1}	Final fluidity, poises^{-1}	Increase in fluidity, poises^{-1}	Original fluidity, poises^{-1}	Final fluidity, poises^{-1}	Increase in fluidity, poises^{-1}
			50 hr.				
Congo Corinth CW	2	5.3	11.1	5.8	—	—	—
Chlorazol Blue B	2	4.5	13.0	8.5	—	—	—
Congo Rubine	2	4.3	13.0	8.7	—	—	—
Chlorazol Blue 3B	2	4.6	12.8	8.2	—	—	—
Chlorazol Violet R	2	4.6	11.8	7.2	—	—	—
Oxomine Scarlet B	2	5.0	13.8	8.8	—	—	—
			100 hr.			200 hr.	
Cibanone Orange R	2	4.8	46.0	41.2	—	—	—
Indanthrene Yellow FFRK	2	4.8	45.0	40.2	—	—	—
Indanthrene Yellow G	2	5.0	44.0	39.0	5.0	28.0	23.0
Indanthrene Gold Orange 3G	2	4.8	35.8	31.0	4.8	28.0	23.2
Cibanone Yellow R	2	4.8	51.8	47.0	—	—	—
			80 hr.			160 hr.	
Stilbenedisulfonic acid	1	4.8	38.6	33.8	4.8	19.4	14.6
Blankophor R	1	4.8	43.2	38.4	4.8	25.5	20.7
Pontamine White 2GT	1	4.8	35.2	30.4	4.8	20.1	15.3
Blankophor B	1	4.8	44.0	39.2	4.8	23.1	18.3
Uvitex RS	1	5.6	39.6	34.0	4.8	15.2	10.4

state either by the release of the entire extra energy as fluorescence or by the transfer of part of the energy to another molecule (in the present case cellulose substrate) while the remainder is emitted as fluorescence. The transfer of energy may take place directly because of the close proximity of the brightener to the cellulose or it may occur through the conversion of atmospheric oxygen to an active form which may attack the fiber substance directly or through the formation of H_2O_2 in the presence of moisture in the surrounding atmosphere. Results of the present investigation are in line with this mechanism. Maximum degradation of cellulose takes place during the first 40 hr. of Fade-Ometer exposure or 80 hr. of sunlight exposure, during which the fluorescent compound is being continuously decomposed. At the end of this period, in the majority of cases, the compound present on the substrate ceases to fluoresce. However, even after this stage, tendering of cellulose still continues with increase in duration of exposure. During this later period of exposure, the mechanism suggested above no longer operates. The products of decomposition of the brightener formed on the fiber substance are now responsible for the degradation. In this connection it may be mentioned that unpublished work by Datye [2], in our laboratories, on fading and phototendering behavior of direct dyes indicates that some of these, such as Congo Corinth CW, Chlorazol Blue B, etc., although they do not exhibit any phototendering activity during the first 50 hr. of Fade-Ometer exposure, do bring about considerable

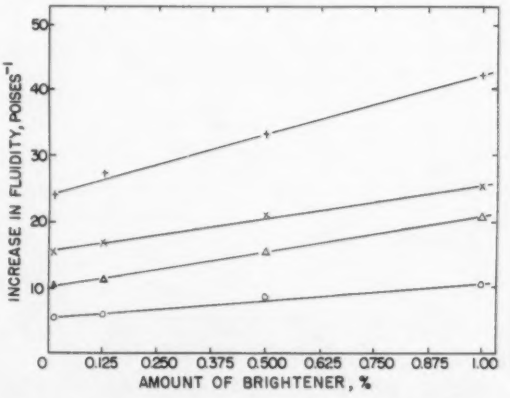


Fig. 12. Relation between increase in fluidity of cotton cellulose and amounts of Blankophor R present on substrate after exposure in Fade-Ometer for different periods. + exposure time 80 hr.; × exposure time 40 hr.; △ exposure time 20 hr.; ○ exposure time 10 hr.

tendering of cellulose when the period of exposure is extended to 100 hr. This goes to show that these direct dyes are not themselves tenderers but that the decomposition products of these dyes accelerate photochemical tendering of cellulose. As most of the brighteners studied have constitutions similar to direct dyes without the chromophore groups, it is very likely that the decomposition products formed during exposure may have similar characteristics. In the absence of any data regarding the nature of the decomposition products formed, it is difficult to suggest a mechanism for their action as photochemical accelerators in the tendering of cellulose.

Study of the Products of Photochemical Degradation of Cellulose by Fluorescent Brighteners

Reduction in bursting strength, increase in cuprammonium fluidity, increase in copper number, and rise in carboxyl content of the exposed brightened samples all indicate that cellulose fiber substance treated with the fluorescent compounds studied undergoes considerable chemical change during exposure. With direct cotton dyes, photo-tendering of the dyed cellulose substrate during exposure has been associated with an oxidative reaction in which cellulose is oxidized to its oxidation products either during the oxidation of the dye by the energy supplied by UV light by a mechanism of auto-oxidation or, in some cases, through the action of activated oxygen or H_2O_2 formed during the oxidation of the dye [3]. It is likely that similar mechanisms may hold good with fluorescent compounds, the main difference being the greater extent of degradation in this case due to the higher capacity of these compounds to absorb light in the UV region. In order to test whether the high values of cuprammonium fluidity for the exposed samples recorded in the present work were real or were fictitious and due to the formation of alkali-sensitive oxycelluloses which would depolymerize during dissolution in the basic cuprammonium hydroxide solvent, these oxycelluloses were reduced under standard conditions with sodium borohydride, a treatment which has been known to stabilize the alkali-sensitive 1:4-glucosidic linkages in the cellulose chain molecule. It was found that fluidity values for oxycelluloses before and after borohydride treatment were the same, indicating a definite reduction in the cellulose chain length. Furthermore, the supposition that these fluidity values are real is substantiated by the observation that reduction in bursting strength is proportional to the increase in fluidity value and that a linear relationship has been found to exist between these two parameters for different conditions of experiment, *viz.* different compounds, varying concentrations of the brightener on substrate, and different times of exposure (Figure 13). Rise in cuprammonium fluidity and increase in the copper number of samples after exposure exhibit a smooth relationship (Figure 14). The carboxyl content of these oxycelluloses does not show a rise proportional to the increase in fluidity or copper number. For instance, although the fluidity values of cotton cellulose containing 1% Blankophor R, Blankophor B, and Pontamine White 2GT increase after exposure in the Fade-Ometer for 80 hr. from 4.8 to 40, 39, and 34 poises^{-1} respectively and the copper number from 0.02 to 2.24, 2.53, and 2.02, the values for the carboxyl content of these oxycelluloses increase only from 0.82 to 2.32, 2.1, and 1.36 meq./100 g. bone dry sample respectively. This may be attributed to the simultaneous decarboxylation of —COOH groups formed during exposure under the experimental conditions with the result that the final values for carboxyl content are comparatively low. A detailed study of the products of the photochemical degrada-

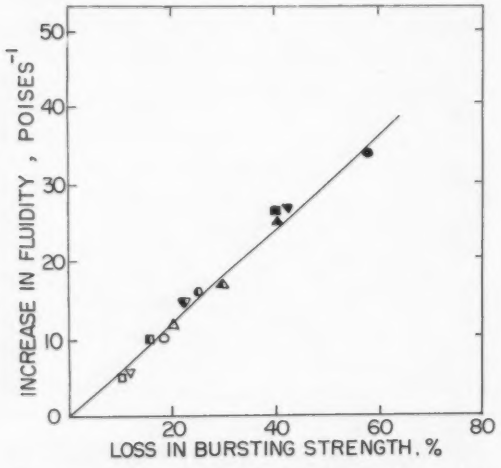


Fig. 13. Relation between increase in fluidity and loss in bursting strength of cotton cellulose containing brighteners after exposure in Fade-Ometer for different periods. Solid dark symbols = 80 hr. exposure; semi-dark symbols = 20 hr. exposure; light symbols = 10 hr. exposure. ○ Blankophor B; □ Uvitex RS; ▽ Pontamine White 2GT; △ Blankophor R.

tion of cellulose treated with fluorescent compounds and exposed to UV radiation is in progress.

In conclusion, it is necessary to point out that in actual practice such high proportions of fluorescent brighteners are not obtained on cellulosic textiles during optical bleaching and thus the tendering effect as recorded in the present work may not be a serious danger in the optical brightening process. However, it should be remembered that most of the present-day brighteners have considerable substantivity to cellulose and 50 to 60% of the compound remains on the substrate even after laundering. It is very likely that at each stage of washing, additional brightener is deposited on the fabric with the result that at the end of several launderings, an appreciable amount of the brightener may be built up on the fabric. Under these conditions, the photo-tendering effect of the brightener may become operative to an appreciable extent, resulting in the loss of essential fiber properties.

Summary

Exposure of fluorescent compounds in aqueous solutions or on cellulose substrate to carbon-arc or solar radiation results in the photodecomposition of the compound to an extent which depends on the chemical constitution of the compound, the nature of the radiation, and the duration of exposure. With all the brighteners studied, absorption in the 300–350 mμ range decreases appreciably after exposure, and the products of decomposition in some cases are yellowish to brown in color and do not fluoresce. Except for diaminostilbenedisulfonic acid, a linear relation has been obtained for the reduction in absorption in the 300–350 mμ region and the fluorescence intensity of a brightener after exposure.

Simultaneous with the photodecomposition of the brightener during exposure, the bursting strength of the material is diminished, the cuprammonium fluidity of the brightened substrate increases, and the copper number also shows a considerable rise, the extent of degradation depending on the amount of brightener present on the substrate, the type and duration of radiation, the chemical constitution of the brightener, and the nature of the substrate. In general, a correlation has been found to exist between fluorescence decay of the brightener on the substrate and the extent of tendering brought about; those compounds which decompose more readily also bring about enhanced tendering.

With all the brighteners studied, even after the stage when the fluorescing capacity of the compound has been destroyed through exposure, degradation of fiber substance continues when the time of exposure is extended, indicating that not only the fluorescent compounds themselves, but also their photodecomposition products are effective in bringing about the breakdown of cellulose chain molecules.

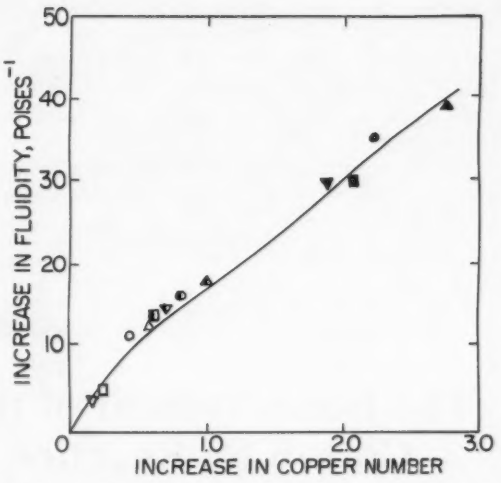


Fig. 14. Relation between increase in fluidity and increase in copper number of cotton cellulose containing different amounts of Blankophor R after exposure in Fade-Ometer for different periods. Solid dark symbols = 80 hr. exposure; semi-dark symbols = 20 hr. exposure; light symbols = 10 hr. exposure. △ Brightener content 1.0%; ○ brightener content 0.5%; □ brightener content 0.15%; ▽ brightener content 0.015%.

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The Improvement of the Wrinkle Recovery of Cotton by Reaction with Formaldehyde[1]

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Abstract

Data are presented showing the reaction of formaldehyde with cotton fabric using phosphoric acid, magnesium chloride, and zinc nitrate as catalysts and the improvement in wrinkle recovery of the fabric obtained by these treatments. A theoretical equation which fits the relationship between improvement in wrinkle recovery and concentration of formaldehyde reacted with cotton was derived which suggests that only part of the reacted formaldehyde is involved in the cross-linking of cellulose molecules.

Introduction

There have been many studies on the reaction of formaldehyde and cellulose, as indicated by the papers of Roff [21] and Marsh [15]. As suggested by several authors and emphasized by the studies of Wagner and Pacsu [27] and Steele [24], the reaction involves, to some extent at least, the formation of a cellulose methylene ether, Cell-O-CH_2-O-Cell, involving two anhydroglucose units (Cell-OH) in two separate molecules [18]. Such a reaction would most probably occur in two steps (disregarding the function of the catalyst which is required for the reaction) which may be represented by the equations

$$CH_2(OH)_2 + \text{Cell—OH} = \text{Cell}\,OCH_2OH + H_2O \quad (I)$$

$$\text{Cell—}OCH_2OH + \text{Cell—OH} = \text{Cell—}OCH_2O\text{—Cell} + H_2O \quad (II)$$

[1] Based on a paper presented at the 137th meeting of the American Chemical Society, Cleveland, Ohio, April 7, 1960.

The possibility of a two-step reaction which in turn must be competitive with the evaporation of formaldehyde [12] makes the quantitative study of the fixation of formaldehyde on cellulosic fibers a somewhat complicated process [29, 30]. Many different catalysts and procedures for applying formaldehyde to cellulose have been used with varying degrees of success [21]. The estimation of the degree of success actually attained is difficult because in most of the previous work no careful distinction was made between the formaldehyde applied to the fiber or fiber assembly and that reacted with the fiber molecules, nor between the total formaldehyde durably fixed to the fiber and that portion which has cross-linked cellulose molecules as indicated by the alteration in the mechanical properties of the fiber [3, 18]. The determination of both the amount of formaldehyde fixed to a fabric and the alteration of properties such as wrinkle recovery or water of imbibition of the same fabric is required [16].

It is the purpose of this paper to report data on the reaction of various amounts of formaldehyde with a cotton fabric and the effect on the wrinkle recovery of the fabric and to analyze these data on the basis of a possible mechanism for the process involved in the chemical modification of cellulosic fibers.

Experimental

The cotton fabric was all from the same batch of non-mercerized plain finished 80 × 80 cotton print cloth prepared for dyeing. It contained no bluing or optical bleach.

Baker and Adamson's Reagent Grade Formalin (37%) was used as the source of formaldehyde. One-yard swatches of the cotton print cloth were treated by padding through formaldehyde solutions containing the catalyst. The pressure on the pad rolls was adjusted to give a wet pick-up of 85%. The solutions were adjusted in concentration to give the amount of formaldehyde and catalyst on the fabric listed in Table I. The treated fabrics were first dried at 107° C. for 0.8 min. and cured as indicated in Table I.

After curing, the fabrics were subjected to a wash consisting of padding through a solution containing 0.25% of Deceresol[2] P Special anionic agent and 0.25% soda ash at 38–43° C. The fabrics were then rinsed four times in running water at 38–43° C. and dried for 0.8 min. at 107° C.

Wrinkle recovery measurements were made using the wrinkle recovery tester following the tentative AATCC test method 66-1956 [1].

Total formaldehyde reacted with the fabric was determined by a hypoiodite procedure [23] after a phosphoric acid digestion of the treated fabric. The free formaldehyde and methylol formaldehyde contents of the fabrics were also determined and found to be the same, within experimental error, as those of the original untreated cotton fabric. The free formaldehyde was determined by a modified sulfite method [17], the methylol formaldehyde by a methylation procedure [17].

Results

The application and the results obtained on the fixation of formaldehyde to 80 × 80 print cloth are summarized in Table I

It will be noted that three catalysts were employed: phosphoric acid, magnesium chloride, and zinc nitrate. Phosphoric acid is a commonly used acid catalyst [18]. The metal salts like magnesium chloride and zinc nitrate are commonly used at present for the reaction of wrinkle resistant finishes for cotton. Metal salts or salts with acids were used in some of the previous work [6, 11, 20, 10]. In general, the metal salts used in this work were more

[2] Reg. U. S. Pat. Office—American Cyanamid Company.

TABLE I. The Application of Formaldehyde to Cotton Print Cloth and the Improvement in Wrinkle Recovery

Catalyst	Catalyst, conc.*	Cure conditions: Time, min.	Cure conditions: Temp., ° C.	% HCHO (on wt. fab.): Applied	% HCHO (on wt. fab.): Combined	Wrinkle recovery, degrees [1]
None	—	—	—	0	0.05†	150
$MgCl_2$	12.0	2.2	177	1.0	0.084	194
H_3PO_4	‡	2.2	177	9.0	0.093	208
H_3PO_4	**	1.5	165	5.0	0.52	212
H_3PO_4	††	3.6	177	9.0	0.58	211
$Zn(NO_3)_2$	8.0	1.5	165	5.0	1.02	245
$MgCl_2$	16.0	1.5	165	5.0	1.15	246
$Zn(NO_3)_2$	16.0	1.5	165	5.0	1.57	260
$Zn(NO_3)_2$	4.0	2.2	177	9.0	1.65	254
$MgCl_2$	16.0	1.5	165	13.0	1.80	260
$MgCl_2$	4.0	1.5	177	9.0	1.89	262
$Zn(NO_3)_2$	8.0	1.5	165	13.0	2.76	259
$MgCl_2$	12.0	2.2	177	17.0	3.09	268

* % on weight of formaldehyde applied.
† Blank applied to obtain combined formaldehyde on treated fabric given in succeeding values in column.
‡ To pH = 2.8.
** To pH = 2.2.
†† To pH = 2.4.

effective than phosphoric acid under the conditions employed. The experiments were designed, however, to obtain a range of concentrations of formaldehyde reacted with cotton rather than to determine the most efficient way of reacting formaldehyde with cellulose. A wide range of concentrations was obtained as indicated by the data in Table I. The effect of these various concentrations of formaldehyde on the wrinkle recovery of cotton is shown in the last column of Table I. These data were studied to determine what they might indicate regarding the nature of the reaction of formaldehyde which results in the wrinkle recovery improvement of cotton fabric.

In Figure 1 the improvement in the wrinkle recovery of cotton (ΔW) is plotted against the concentration of formaldehyde combined with the fabric (R_o) expressed in millimoles per 100 grams cotton.

The data in Figure 1 can also be represented in a linear form by plotting the concentration of reacted formaldehyde divided by the wrinkle recovery improvement of cotton ($R_o/\Delta W$) against R_o as shown in Figure 2. Thus, the data for the improvement of the wrinkle recovery of cotton obtained by various concentrations of reacted formaldehyde correspond to the empirical relationship

$$R_o/\Delta W = BR_o + C \qquad (1)$$

This empirical relationship may be of value in itself, especially since other cellulose reactants show the same or similar relationships between improvement in wrinkle recovery of cotton and the concentration of chemically reacted compound [5, p. 155]. Since the relationship expressed by Equation 1 may be

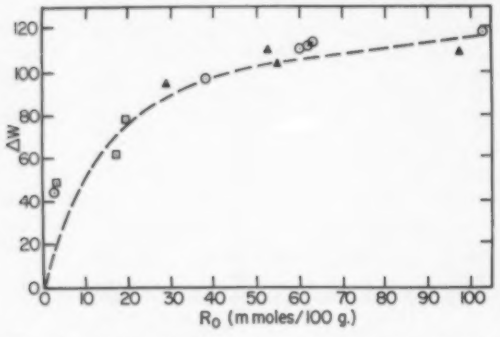

Fig. 1. A plot of the wrinkle recovery improvement of cotton (ΔW) against the molar concentration (R_o,mmoles/100 g. fabric) of formaldehyde reacted with the fabric using phosphoric acid, □; zinc nitrate, △; and magnesium chloride, ○; as catalyst.

generally applicable to cellulose reactants it may represent more than a chance relationship. This suggests that it would be worth while to consider the factors involved in the modification of the mechanical properties of cotton which might lead to Equation 1.

General Considerations Regarding Cross-Linking

If the cross-linking of cellulose molecules which modifies the properties of cotton involves only the amorphous cellulose, the cross-linking should be similar to that occurring in other amorphous polymers [8, 9]. It should occur at randomly selected sites governed by the laws of chance. While the cross-linking is a random process it does not involve the random selection of pairs of anhydroglucose units. Cross-linking will occur where the molecules are oriented so that a glucose residue of one molecule is in an adjacent position to a similar unit in a neighboring molecule.

Considering, also, that the mechanical properties of an amorphous polymer like rubber are modified drastically by a relatively few cross links, it may be that only a relatively few cross links between amorphous cellulose molecules are responsible for the improved wrinkle recovery of cotton. In the amorphous region this may also be true for the hydrogen bond cross links which contribute to the recovery of unmodified cotton. The wrinkle-recovery-improvement–formaldehyde-concentration data presented in this paper indicate that significant wrinkle recovery improvement is obtained when the amount of reacted formaldehyde is sufficient to produce about 150 cross links for every pair of cellulose molecules in the amorphous region and that the amount of formaldehyde (3%) reacted as the limiting degree of wrinkle recovery is approached, indicated by the levelling of the curve in Figure 2, corresponds to about one cross link for every pair of anhydroglucose units in the amorphous region or about 1500 cross links for each amorphous molecule. On the basis of the analogy with other amorphous polymers it appears quite unlikely that so much cross-linking is necessary to produce the observed modification of the properties of cotton even if it were possible. Since essentially all of the formaldehyde reacted with the fabric is present as the acetal, as shown by the analysis of the treated fabrics, all of the formaldehyde must be accounted for in the form of a methylene ether bridge. The work of Wagner and Pacsu [27] indicates that these bridges

are all intermolecular bridges or cross links. Wood [31, 32] and more recently Roff [21] have suggested that intramolecular bridges may be formed. Steele [25] has suggested that differences in the wet and dry wrinkle recovery values of different fabrics may be due to different proportions of intermolecular and intramolecular bridges. In the derivation of a theoretical equation, then, the possibility of both cross links and intramolecular bridges of some kind should be considered.

Theoretical Wrinkle Recovery–Concentration Relationship

In the work summarized in Table I, the reaction of formaldehyde with cellulose occurs after padding and drying and during the baking operation. During the padding, the formaldehyde in solution is adsorbed as indicated by Roff [22]. During the drying and baking, some formaldehyde is lost by desorption and evaporation. The solvent is removed in a very short time. During this time, the cotton contracts and the formaldehyde adsorbed by the cellulose enters into reaction with cellulose as indicated by Equations I and II. The first step of the reaction (Equation I) is undoubtedly rapid compared with the second step. All of the formaldehyde which becomes durably reacted with the cellulose must first form the hemiacetal. The initial concentration of hemiacetal for the second step of the reaction is equal to the total concentration of chemically reacted formaldehyde, R_0.

The second step of the reaction is the rate-determining step. It may be likened to the Langmuir adsorption process [15] in that it involves interaction at certain sites. In Equation II HO-Cell represents the n anhydroglucose units per unit weight of cotton which serve as cross-linking sites. The rate of the forward reaction will be proportional to the concentration of reacted formaldehyde in the form Cell-OROH and the fraction of the n sites not yet involved in cross-linking. The rate of the reverse reaction will be proportional to the number of cross links formed and the partial pressure or concentration of water. That is

$$dx/dt = k_1(R_0 - C_x)n(1 - x) \qquad (2)$$

$$dx/dt = k_2 nx p\mathrm{H_2O} \qquad (3)$$

In these equations R_0 is the concentration of formaldehyde reacted with cellulose. C_x is the concentration of formaldehyde and x is the fraction of available cross-linking sites involved in cross-linking. p is the partial pressure of water. At equilibrium

$$k_1(R_0 - C_x)(1 - x) = k_2 x \cdot p\mathrm{H_2O} \qquad (4)$$

Equation 4 is a relationship between the concentration of reacted formaldehyde and cross-linking. What is desired, of course, is a relationship between the concentration of reacted formaldehyde and wrinkle recovery improvement.

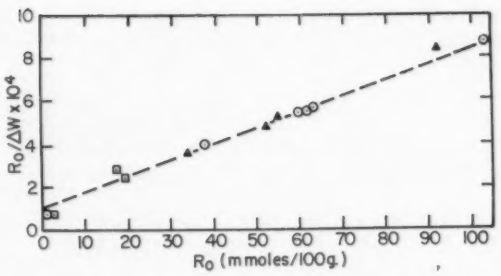

Fig. 2. A plot of R_0 ΔW against R_0 for the interaction of cellulose with formaldehyde using phosphoric acid, □; zinc nitrate, △; and magnesium chloride, ○; as catalysts.

Wrinkle recovery improvement is related to elastic recovery [4, 10]. For example it has been shown [4] that wrinkle recovery improvement is approximately proportional to the elasticity of a fabric or of the yarns or fibers from which it is made, elasticity being defined as the recovery from a given strain in an arbitrary time interval such as 5 min. The improved elasticity of cotton is, of course, attributed to the cross-linking of cellulose molecules. Since the cross-linking is considered to occur primarily in the amorphous region of the cellulose [30] the relationship between cross-linking and the elastic properties of cotton might be similar to that for other amorphous polymers such as rubber for which the retractive force at a given elongation is directly proportional to the number of random cross links formed [2, 8]. While the retractive force and elastic recovery are not identical properties they are closely related, at least at low extensions. As a first approximation, then, the assumption is made that wrinkle recovery improvement is directly proportional to the number of cross links formed as expressed by the equation $\Delta W = Kx$ where K is a proportionality constant. When all of the available cross-linking sites are utilized, that is when $x = 1$

$$\Delta W = \Delta W_L = K \qquad (5)$$

where ΔW_L is the limiting wrinkle recovery im-

provement obtainable. On the basis of this approximation the fraction of sites involved in cross-linking is expressed by

$$x = \Delta W/\Delta W_L \tag{6}$$

Substitution of Equation 6 into Equation 4 gives, after algebraic rearrangement the equation,

$$\frac{(R_0 - C_x)}{\Delta W} = \frac{(R_0 - C_x)}{\Delta W_L} + \frac{k_2 p}{k_1 \Delta W_L} \tag{7}$$

Equation 7 differs from the empirical equation only in the formaldehyde and water concentration term. The two equations become approximately identical if p is a constant and if C_x is small in comparison with R_0. That is if

$$p = \text{a constant};\ C_x \ll R_0$$

$$R_0 = C_x \equiv R_0$$

$$\frac{R_0}{\Delta W} = \frac{R_0}{\Delta W_L} + \frac{A}{\Delta W_L} \tag{7a}$$

This of course is identical with the empirical Equation 1 with the slope of the line

$$B = 1/\Delta W_L$$

and the intercept $C = A/\Delta W_L$ and $A = k_2 p/k_1$.

Under hot, dry conditions of application precautions are not usually taken to insure that the partial pressure of water is constant. The partial pressure of water is low, however, and in the short time intervals involved, 1.5 min. with a steady flow of air, it is not likely to vary significantly. If the reaction is carried out under wet conditions which involves either a relatively large volume of water [19] or a reaction in a closed system, the concentration of water is approximately constant.

The requirement that C_x be negligible with respect to R_0 implies that only a small fraction of the formaldehyde reacted with cellulose is involved in cross-linking cellulose molecules. This in turn requires that the major fraction of the reacted formaldehyde molecules form intraunit or intrachain bridges of some sort, perhaps like those suggested by Wood [31] and Roff [21]. The conclusion, that only part of the reacted formaldehyde is involved in the cross-linking of cellulose, which is required to reconcile the above theory with the experimental wrinkle recovery improvement–concentration relationship is apparently but not necessarily in contradiction with the widely accepted concept of complete cross-linking of amorphous cellulose, which has received its best support from the chemical study made by Wagner and Pacsu [27]. The conclusion regarding intermolecular bonding is generally derived indirectly from a consideration of the tensile properties of formaldehyde reacted cotton. It is possible, as suggested above, that the mechanical properties of the treated cotton could be accounted for if only a fraction of the formaldehyde were involved in intermolecular reaction. The conclusion regarding the type of chemical bonding of a cotton structure made elastic or wrinkle resistant by reaction with cellulose was also derived indirectly. Unfortunately, Wagner and Pacsu did not report data on the textile and tensile properties of the formaldehyde treated cotton obtained in their study. It is possible that the product containing about 6% of reacted formaldehyde obtained by their method is different from the wrinkle-resistant cotton obtained by the procedures employed in this work, which give an upper limit of about 3% reacted formaldehyde based on the weight of cotton. As pointed out above, 3% formaldehyde is sufficient to produce one cross link for each pair of amorphous anhydroglucose units in cotton, assuming the amorphous content to be 30%. Higher concentrations of formaldehyde might lead to an entirely different product which would probably involve, to some extent at least, the crystalline region of cellulose. A process leading to such a high degree of substitution might be expected to produce a more profound effect on the cotton structure than that produced by those methods of applying formaldehyde which produce cotton fabrics known to be wrinkle resistant. Thus the possibility that in formaldehyde treated cotton fabrics known to have wrinkle recovery the presence of intraunit as well as cross links is not completely ruled out.

Because of the similarity of the reaction of formaldehyde to those of other cross-linking agents already observed [3, 4, 14, 15], it is very probable that the concepts developed here are generally applicable to reactions of cellulose and cross-linking agents including, perhaps, some reactive dyes [26].

The data presented by Marsh [15] indicate that these concepts apply to rayon as well as to cotton and that the change in the water of imbibition of the fabric may be treated in the same way as wrinkle recovery.

Water of imbibition, of course, is related to swelling of the amorphous cellulose, and swelling is a function of cross-linking. If as a first approxima-

tion, the change (decrease) in water of imbibition is taken to be directly proportional to the extent of cross-linking, an equation can be derived which corresponds with that describing experimental data. For example, the data of Daul [7] on the change in the water of imbibition of rayon as a function of the concentration of reacted cross-linking agent fit an equation like Equation 1 for a number of cross-linking agents. The data for the formaldehyde–rayon system fit the equation

$$R_0/\Delta Wi = 0.0104R_0 + 0.0021$$

where ΔWi is the change (decrease) in the water of imbibition of rayon due to reaction of formaldehyde and R_0 is the total concentration of formaldehyde (moles/100 g. fabric) reacted with the fabric; the constants were evaluated by the method of least squares. This of course is similar to Equation 1 and a theoretical equation corresponding to Equation 7 can be derived by replacing Equation 5 with $x = \Delta Wi/\Delta Wi_L$ where x is the degree of cross-linking, ΔWi is the decrease in the water of imbibition, and ΔWi_L is the limiting decrease in water of imbibition which would be approximately equal numerically to the water of imbibition of the untreated fabric.

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Fourth Meeting

Polymer and Fiber Microscopy Society

(Sponsored by Textile Research Institute)

Treadway Inn, Norwalk, Connecticut, Thursday and Friday, May 11 and 12, 1961

Those interested in attending may address their inquiries to T. G. Rochow, Program Chairman, American Cyanamid Co., Stamford, Conn.

Thursday Morning. Chairman: F. F. Morehead, American Viscose Corp.

9:30 Opening Remarks by Program Chairman, T. G. Rochow, American Cyanamid Co.

9:35 G. L. Royer, Stamford Research Labs., American Cyanamid Co., "Needs of Microscopists and Needs of Management for Microscopy"

10:15 O. W. Richards, American Optical Co., "Seeing Problems of Visual Microscopy"

11:00 P. Bartels, E. Leitz, Inc., "Photomicrography of Fiber and Polymer Surfaces"

11:30 S. B. Newman, National Bureau of Standards, "Simple Physical Methods for Producing Contrast in Fibrous Structures"

Thursday Afternoon. Chairman: A. Coe, Textile Research Institute

2:00 S. E. Summers and E. F. Fullam, Ernest F. Fullam, Inc., "A Study of a Textile with Electron, Light, and X-ray Microscopy"

2:30 W. D. Niegisch, Union Carbide Plastics Co., "The Morphology of Crazing in Some Amorphous, Thermoplastic Polymers"

3:15 R. J. Clark and G. C. Claver, Monsanto Chemical Co., "Micromorphology of Heterogeneous Polymers"

3:45 P. H. Geil, and R. G. Scott, E. I. du Pont de Nemours & Co., "Morphology of Polymer Crystals"

4:15 N. K. J. Symons, E. I. du Pont de Nemours & Co., "Crystals of Polytetrafluoroethylene Grown from Solution

* * *

7:00 Dinner Speaker: H. R. Cox, Director of Virus and Rickettsial Research, Lederle Div., American Cyanamid Co., "Oral Vaccine Against Poliomyelitis"

Friday Morning. Chairman: R. G. Scott, E. I. du Pont de Nemours & Co.

9:00 V. F. Holland, Chemstrand Research Center Corp., "Microscopical Studies of Fractionated Polyethylene"

9:30 F. F. Morehead, American Viscose Corp., "Microstructure of Viscose Rayon"

10:15 M. Wishman, F. E. Detoro, M. C. Botty, C. D. Felton, and R. E. Anderson, American Cyanamid Co., "Microscopical Studies of Polymerization Initiation"

10.:45 C. D. Felton, M. C. Botty, and J. Clark, American Cyanamid Co., "Microscopical Techniques for the Investigation of the Structure of Paper"

2:00 Visit to American Cyanamid's Central Research Laboratories. Tour of areas including Polymers, Resins, Fibers, and Microscopy.